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METHODS AND PROCEDURES USED IN THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY PROGRAM OF INVESTIGATION OF THE PRESSURES AND VOLUMES OF WATER TO 460° C.

PART I.

BY FREDERICK G. KEYES.

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PART I.

By Frederick G. Keyes.

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 299.)

METHODS AND PROCEDURES USED IN THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY PROGRAM OF INVESTIGATION OF THE PRESSURES AND VOLUMES OF WATER TO 460° C.

PART I.

By Frederick G. Keyes.

(Read by title October 11, 1933.)

(1) Introduction.

Somewhat over a decade ago the extremes of the ranges in pressure and temperature of the experimentally determined properties of steam,[1] excepting the saturation pressure-temperature relation, did not exceed eleven atmospheres and 40° C of superheat. The urgent need of a more extended and highly exact knowledge of the properties of water, required for steam boiler and turbine design, resulted at the instance of Mr. George A. Orrok in the bringing together in June 1921 of a group of engineers and scientific men for the discussion of a comprehensive program of research. The group of fourteen, meeting at Harvard University, included important users of steam, several compilers of steam tables, a number of experimental experts and the chairmen of the three A. S. M. E. committees.[2] As a result of the extended discussion and exchange of views a program of investigation was planned to be carried out in three institutions. The U. S. Bureau of Standards was to undertake the measurement of quantities such as the heat function $H = U + pV$ for the liquid phase, and heats of evaporation. The pressure, volume, temperature relations of water over as extended a range of the variables as the most modern facilities would permit was to be carried out at the Massachusetts Institute of Technology. The measurement of the Joule-Thomson effect over

[1] Amagat, Ann. de Chim. et de Phys. *29*, 545 (1893) had measured the volumes of liquid water over a limited range of temperature to 3000 atms. and a more extended temperature range to 1000 atms. The data had never been used for incorporation in steam tables, however, before Joseph H. Keenan's formulation of the "Thermal Properties of Compressed Liquid Water," Mech. Eng. *53*, 127 (1931).

[2] Mech. Eng. *43*, 557 (1921).

wide ranges of pressure and temperature was to take place at the Harvard Engineering School. The final results of the investigations conducted under these three main divisions of the program were to supply a variety of data which, through the use of the two empirical principles of thermodynamics, could be interrelated and assurance provided that the consistency of the entire mass of experimental findings was satisfactory.

Reports of experimental findings have been presented in the Steam Tables Conferences at the yearly December meetings in New York City of the A. S. M. E. and the reports published in Mechanical Engineering.[3] These reports naturally constitute records of progress, provisional correlations, discussions of difficulties encountered and suggestions bearing on the means by which obstacles encountered were to be surmounted. The annual meetings have been in fact a sort of "clearing house" for the accumulating facts and information bearing on steam properties and have proved a most valuable feature of the comprehensive steam research program.

Interest in a more extended knowledge of the thermodynamic properties of water has also prompted investigations abroad, notably by H. L. Callendar, G. S. Callendar, and A. C. Edgerton in England, Jacob and Fritz, Knoblauch, Koch and others in Germany, and Havlíček and Zvoníček in Czechoslovakia. Committees were organized in these countries and in collaboration with the American Committee on Steam Research an international conference was held in London on July 8, 1929, to discuss the steam investigations. During the five days over which the Conference extended a "skeleton" table of thermodynamic properties was agreed upon. The latter table[4] consists of a set of selected fixed points in the saturated and superheated regions accompanied by an estimate of the reliability of each datum. It was also agreed in the conference that if at each of the points given in the Conference Table any existing table of steam properties lay within the estimate of reliability, then the latter was to be considered an "International Table" of steam properties. It was expected that the international fixed points tabulation would be revised in further conferences and a second international conference[5]

[3] Mech. Eng. *45*, 165 (1923); *46*, 81 (1924); *47*, 103 (1925); *48*, 151 (1926); *49*, 161 (1927); *50*, 152 (1928); *51*, 109 (1929); *52*, 124 (1930); *53*, 132 (1931); *54*, 118 (1932); *55*, 113 (1933).

[4] Mech. Eng. *52*, 120 (1930).

[5] Mech. Eng. *53*, 289 (1931).

was held in Berlin in June, 1930. The third conference is to be held in the United States at a time not yet definitely selected.

(2) Purpose of the Present Paper.

The present paper is the first of a series of papers and contains the detailed record of the experimental procedures and methods employed to obtain the data recorded in the succeeding papers. More than ten years of effort have been expended in experimentation and no resource has been neglected to develop apparatus and technique capable of yielding precise data on the pressure, temperature and volume properties of the liquid and vapor phases of water. The pressures have extended to more than 300 atmospheres. The temperature of experiment has been carried to 460°, and volume measurements have been made throughout the pressure and temperature ranges stated, including practically the whole of the saturation region. It is proposed in the papers to follow not only to present the experimental data obtained but to correlate the new data with the older body of water data and the results obtained by our American collaborators in the A. S. M. E. Steam Program,— N. S. Osborne, H. F. Stimson, and E. F. Fioch working at the U. S. Bureau of Standards; and H. N. Davis and R. V. Kleinschmidt who carried out the Joule-Thomson experiments at the Harvard Engineering School. The considerable body of important data obtained abroad is also to be included in the project of correlating all relevant steam data. Finally, certain new direct experimental determinations of $\left(\frac{\partial H}{\partial p}\right)_T$ at low pressures and temperatures are in progress and it is expected that the data will be available for consideration in completing our knowledge of the properties of steam in a region where reliable experimental results are obtained with difficulty by the usual methods.[6]

(3) Experimental Background for the Work.

The project of measuring the pressures and volumes of liquid water and water vapor or steam was by no means a new project at the Research Laboratory of Physical Chemistry. William D. Coolidge[7] in 1903 had completed certain important investigations on the conductivity of aqueous solutions to 306° C. In the course of interpreting

[6] F. G. Keyes and S. C. Collins, Proc. Nat. Acad. Sci. *18*, 328 (1932).

[7] A. A. Noyes and W. D. Coolidge, Proc. Am. Acad. Arts and Sci. *39*, 163 (1903).

and correlating the data Coolidge had found the need of exact volume data for water at higher temperatures. The apparatus for new and extended measurements of volumes and pressures was accordingly designed and constructed. Actual measurements were carried out by R. D. Mailey, in 1910, using a Bourdon gauge for the pressure measurements. At about this time I undertook to determine the physical properties of Ammonia and adopted the Amagat "dead weight" or piston type of pressure gauge which has evolved under gradual development into the form which for purposes of distinction may be designated the Research Laboratory of Physical Chemistry type of absolute gauge.[8] Mr. Mailey redesigned the volume measuring portion of his apparatus and, using the piston gauge but retaining the platinum lined container previously used, made a series of measurements on water in 1912. These measurements were of a preliminary character and have never been published. The data and experience gained, however, have been of the greatest value and constitute a part of the background of the present methods and procedures herein described.

The measurements of the vapor pressure of water by Holborn and Baumann[9] as well as R. D. Mailey's work had indicated that water in contact with steel may under certain conditions give rise to permanent gas evolution at temperatures above 300° C. Such interaction of container material and water is a serious obstacle to accurate measurements of the pressure of water. Of course it has long been known that at a red heat iron becomes oxidized by steam yielding iron oxide and hydrogen, and Coolidge selected platinum as the container. A sphere of platinum from a single sheet was spun over a hard wood mould and the wood subsequently burned out. The sphere was then placed in a steel retaining shell consisting of two hemispheres so designed that they just enclosed the platinum hemispheres when screwed together. The neck of the platinum shell was spun back perpendicular to its axis and used as the seat for a gold gasket closure. Copper capillary tubing was used to connect the platinum sphere to the volume measuring device. The sphere was loaded with water by placing the end of the copper capillary below the surface of a quantity of boiling distilled water held in a glass flask

[8] F. G. Keyes and Jane Dewey, Jour. Optical Soc. Am. *14*, 491 (1927). J. A. Beattie and W. L. Edel, Ann. Physik, *11*, 633 (1931). J. A. Beattie and O. C. Bridgeman, Ann. physik, *12*, 827 (1932).

[9] Holborn and Baumann, Ann Physik, *31*, 945 (1910).

and applying heat to the platinum lined container. Water was repeatedly driven into the container by heating and cooling the latter until it was judged to be loaded with air free water.

The defect of a platinum lined or compound container is that its volume is a complicated and apparently erratic function of the pressure and temperature. The difficulty of obtaining a "perfect" fit of the platinum lining to the interior of the steel retaining shell is in fact quite serious. The coefficient of thermal expansion of the platinum, moreover, is smaller than that of steel so that a fit at one temperature could not insure a fit at another temperature. By means of pressure applied within the container the platinum lining can be forced into contact with the steel container but the inherent elastic properties of platinum requires that the relation between the volume of the container and the pressure involve a sort of discontinuity occurring at the point where the platinum shell yields and settles exactly into the steel retaining sphere. The pressure-volume properties of the container space can be made fairly reproducible at constant temperature since the elastic yielding of the lining will come to a fairly definite value as the application and release of pressure is repeated. On considerable change of temperature however the latter condition is upset for the platinum becomes annealed if the change is to higher temperatures and thus it is perceived that for measurements aiming at the highest precision the compound container is inferior to a container constructed of a single homogeneous piece of metal.

It is not difficult to predict what metals are most suitable from the point of view of chemical inertness toward water. The *equilibrium* ratio of the pressure of hydrogen to the pressure of steam at the temperature of measurement can in fact be readily computed. Practically it will suffice if this ratio is sufficiently small at the highest temperature of the steam measurements. To compute the ratio there is required the decomposition or equilibrium pressure of oxygen over the oxide of the container material at the temperature of interest and the equilibrium values for the decomposition of steam into its elements, hydrogen and oxygen. For silver interacting with water the oxide of silver is known to be Ag_2O and $2\,Ag + H_2O = Ag_2O + H_2$. The latter is however equivalent to the two equilibria:

$$2Ag + \tfrac{1}{2}O_2 = Ag_2O \qquad (a)$$

$$H_2O = H_2 + \tfrac{1}{2}O_2 \qquad (b)$$

The equilibrium values for reaction (a) and (b) are known and

have been formulated.[10] The ratio pH_2/pH_2O is 7.0×10^{-28} at 150° C and 8.5×10^{-16} at 500° C. These values are small enough to qualify silver as a satisfactory metal from the chemical viewpoint. However, silver is a metal with unsatisfactory elastic properties in the temperature and pressure range over which it was desired to make volume measurements unless a compound or silver lined container was adopted. The early experience available with a platinum container indicated that the compound bomb should be used only as a last resource.

The equilibrium ratio of hydrogen to steam in the case of iron is not as simple as for silver due to the existence of several iron oxides.[11, 12] However for the oxide Fe_3O_4 equilibrium pressures are known and the ratio is computed to be $\frac{pH_2}{pH_2O} = 3.4$ at 500° C. This value and in fact similar values of the ratio for any metal gives the *equilibrium* value. In practice the equilibrium value may not be realized due to the effect of "passive resistance," the entire nature of which is still obscure. The fact is well known that smaller and apparently stationary values of the ratio are likely to be observed, particularly at lower temperatures.

One circumstance which has been frequently observed is that after an initial layer of oxide has formed on the surface of a metal the reaction to form more oxide proceeds much more slowly and may even come to an apparent stop. It must not be overlooked, moreover, that many or rather most metals absorb appreciable quantities of hydrogen and if this is the case the rate of formation of oxide may be comparable with the rate of absorption of hydrogen by the metal under the actual conditions of use of the container. In this event no permanent gas would be present but water would progressively disappear from the container, the oxygen of which it is composed combining with the metal to form oxide and the hydrogen diffusing into the metal.

Something should be stated regarding the preferred mechanical properties of the container material. A pure metal or as nearly pure as can be obtained commercially is desirable because pure metals are generally supposed to possess more regular and reproducible elastic and thermal expansivity characteristics; at least more nearly inde-

[10] Lewis and Randall "Thermodynamics" McGraw-Hill Book Co. 1923.

[11] Eastmen, J. Am. Chem. Soc. *44*, 975 (1922); Eastman and Evans, J. Am. Chem. Soc. *46*, 888 (1924).

[12] Lewis and Randall, loc. cit.

pendent of previous history and treatment, than are most alloys. It is clear, in any event, that it is desirable to use as a container material a substance whose elastic properties have been thoroughly investigated. Unfortunately, elastic behavior has been investigated with any completeness for only a few metals. In the steam investigation these properties were desired over the range from room temperature to 500° C and it was found that the values of Young's modulus[13] and Poisson's ratio[14] are relatively fairly well known for nickel. Because of this and from such indications as could be adduced regarding its actual chemical behavior in the presence of steam it was decided to begin the measurements with a container of this substance. The dissociation pressure of oxygen over nickel oxide NiO is known[15] and the equilibrium ratio of hydrogen to steam is $\frac{pH_2}{pH_2O} = 4.2 \times 10^{-3}$ at 600° and 3.0×10^{-3} at 485°. The fact that nickel does not amalgamate with mercury at ordinary temperatures was also a point favoring the use of nickel.

(4) The Steam Containers Employed.

Young's modulus for nickel in its relation to temperature is shown graphically in Fig. 1, and it is observed that above 425° C the change of the modulus with the temperature is quite abrupt. In fact some physical or quasi-chemical change in the nickel would seem to be indicated, the exact nature of which is still obscure. From the practical point of view it would of course be unwise to use a nickel container above 425° C and measurements were not extended beyond 400° C. The temperature dependance data for Young's modulus may be represented with sufficient fidelity by a linear function (except nickel above 200°) for most metals of the kind that would be considered for use as pressure vessels. Unfortunately however the data available are not impressive either as to quality, quantity, or temperature range. The modulus does however, and the rigidity likewise, diminish with temperature rise and the temperature coefficient of the latter is larger than the former. Thus for nickel below 200°,[16] the Young modulus decreases by 2.47 percent per 100° and the rigidity by 3.28 percent per

[13] E. P. Harrison, Proc. Phys. Soc. London, *27*, 8 (1914).
[14] A. Bock, Wied. Ann., *52*, 609 (1894).
[15] Pease and Cook, J. Am. Chem. Soc., *48*, 1199 (1926).
[16] Schaefer, Ann. Physik, *5*, 220 (1901); *9*, 1124 (1902).

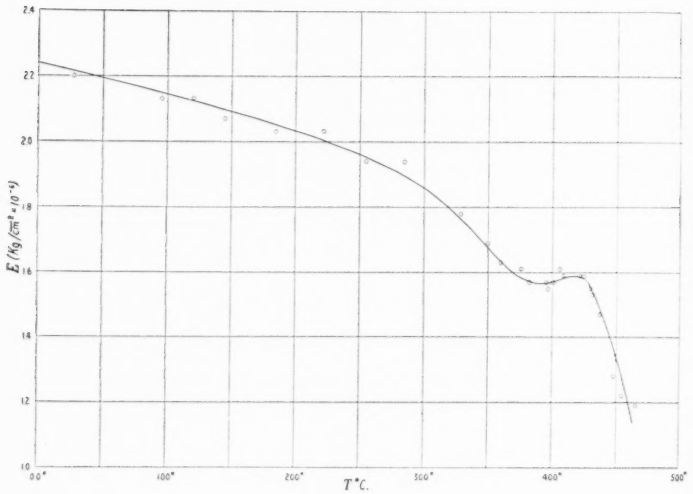

FIG. 1.

100°. From the classical elasticity theory we have, for the relation between Poisson's ratio (σ), Young's modulus (E) and the rigidity (μ):

$$1 + \sigma = \frac{E}{2\mu} = \frac{E_0(1 - \alpha t)}{2\mu_0(1 - \beta t)}$$

or

$$\sigma = \sigma_0 + (1 + \sigma_0)\left[(\beta - \alpha)t + \beta t^2(\beta - \alpha)\frac{1}{1 - \beta t} \right]$$

It is clear from the figures of Schaefer for nickel that part of the second term of the right hand member of the last equation may be neglected since β $(\beta - \alpha)$ is small relative to $(\beta - \alpha)$. This is the case with all metals so far as I can determine and the dependance of Poisson's ratio on temperature for nickel becomes on the basis of Schaefer's data:

$$\sigma = \sigma_0(1 + 8.1 \times 10^{-5}t) + 8.1 \times 10^{-5}t$$

It will be observed that the (0 − 200) data of Harrison for Young's modulus indicate a much higher (54 percent) temperature coefficient than that of Schaefer. The latter, however, measured both coeffi-

cients in the same investigations and the results may be relatively quite exact in which case the temperature dependance deduced for σ would be reliable. In any event the indication is that the variation of σ is smaller than the Young modulus and rigidity modulus, and always positive when the temperature coefficient of the latter exceeds the former. In the case of nickel, $\sigma = 0.33$ was employed in formula 1 and it is a property of the latter equation that it is quite insensitive to variation in σ. The extreme upper value of σ is 0.5 at the melting point and for temperatures of use far lower, as with nickel or steel in

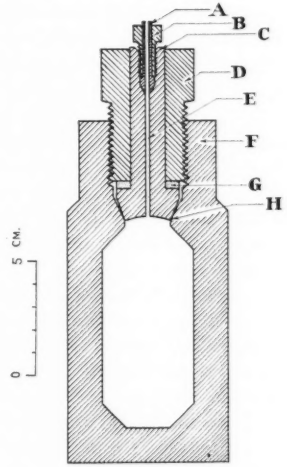

FIG. 2.

the present investigations, the assumption that σ is independent of temperature is often justified.

The form of the first or nickel container is shown in Fig. 2. The material, a special forging, was obtained from the International Nickel Company[17] and was the purest nickel obtainable commercially.

[17] We take pleasure in acknowledging our indebtedness to Mr. H. T. Cole and Mr. H. G. Fales of the International Nickel Company for their interest and helpfulness not only in supplying specially forged pieces of nickel and monel metal but for much special information which proved of the greatest value.

The volume of the completed container was about 220 cc. Closure was effected by a device much used in this laboratory, that of using a cone closure piece *C*, Fig. 2, of nickel of 1½° less angle than the 45° angle cone of the seat machined at the bottom of the threaded neck, *F*. Contact is made at *H* and a bronze slip-ring lubricated with talc used at *G*. The member *D* drives the cone to a pressure tight seat and is of nickel. To connect the container with the measuring apparatus a nickel capillary[18] 0.62 mm. in bore and 2.25 mm. in outside diameter was employed.

The method of connecting with the container was to weld the capillary to the Ni cone *A* at the tip. The resulting slight irregularity produced at the tip of the cone was removed in the lathe and the end drilled to correspond to the bore of the capillary. The cone *A* was seated by means of the threaded driving piece *B*.

The constant temperature bath, to be described later, contained as bath fluid a molten mixture of sodium, potassium and lithium nitrates. Unless the threads of the container are properly lubricated it will be found impossible to disassemble the container after it has once been heated in the molten salt bath. The use of graphite is ineffective because it is completely oxidized during the long course of the heating required during measurements. The lubricant which has been found satisfactory is pure talc in finely powdered form mixed with heavy paraffin oil to a glycerine-like consistency. The mixture is brushed on the threads and the container locked in the usual manner. To open the container after long heating in the bath it is necessary to submerge the container in warm water to soften and dissolve the solidified salt which will be found to have penetrated into the threaded portion and oxidized the paraffin oil. The container is next warmed and oil allowed to enter the threads. After a short time it will be found that the threads may be "started" after which further warming and application of oil, if necessary, may be desirable. By proceeding with reasonable caution, avoiding hurry or forcing, it is possible to open and close the various types of containers repeatedly without harming the threads in the slighest degree. This statement is true not only for the case where the container is of nickel but where it is composed of ordinary low carbon or alloy steel. Cold worked steel, it may be noted, should always be annealed to remove strains before machining.

[18] The nickel capillary we owe to the kindness of Mr. Philip Dorticos of the Edison Lamp Works at Harrison, New Jersey.

A point of no small importance in connection with a container formed from a solid ingot should be stressed. Experience over a period of some twenty years has shown that usually a bar of forged material has one or more fine capillary pores running parallel with the axis for considerable distances formed in the course of the elongation from small pockets or slag inclusions in the interior of the ingot during the forging or rolling operation. The first attempt to obtain a satisfactory nickel container for the steam work resulted in failure due to this kind of a defect. It would be most satisfactory of course to have the forging made from nickel which had been cast *in vacuo* but at the present time this does not appear to be commercially practicable. The successful nickel container of the form of Fig. 2 was finally made from a section of a long piece which had been forged a second time in a direction perpendicular to the original axis. Even this container, after several years use, developed a minute leak through the wall perpendicular to the axis.[19] This appeared however to be due to the progressive crystallization of the nickel to large grain size with attendant weakening of the container. At all events careful examination disclosed to Doctor Smith a fine crack running around the container for some distance. Independent experience has convinced the writer that large crystal grains do form in nickel on prolonged heating at high temperatures. The same phenomenon occurs in the case of tungsten.

The essentially cylindrical form of the nickel container, Fig. 2, was chosen because this form lends itself to simple treatment in determining the increase of the internal volume with pressure. The external form was actually hexagonal except for the neck F. The area of the hexagonal section was used to compute the equivalent radius of a circle of equal section and this radius was used in computing the dilation of the container volume with pressure by means of the formula:

$$\Delta V = V\left[\frac{3(1-2\sigma)}{E}\,\frac{p_i r_i^2 - p_0 r_0^2}{r_0^2 - r_i^2} + \frac{2(1+\sigma)}{E}\,\frac{(p_i - p_0) r_0^2}{r_0^2 - r_i^2}\right] \quad (1)$$

[19] Many years ago during the course of the commercial production of glass mercury arc rectifiers and mercury arc lamps, "epidemics" of leaky units would appear. The difficulty was finally traced to the same cause as has been described in the case of the forged billets used for the steam containers. The platinum wire then used for seals was drawn from ingots which had air bubble inclusions. The remedy in this case was to cut the platinum lead in two and weld the portions together in the oxy-hydrogen flame before using. This is still good practice in the laboratory where platinum wire is used for leads.

where ΔV is the volume displacement when the internal pressure is p_i and the outside pressure is p_0, r_i is the internal radius, E is Young's modulus, and σ Poisson's ratio. The contribution to the total increase in volume due to the ends of the cylinder was approximated by considering the ends to be equivalent hemispheres. The values of Young's modulus and Poisson's ratio used for the nickel container will be found in Table I.

The volume increase with pressure was also determined experimentally by evacuating the container and filling it completely with pure mercury. The apparent compressibility of the mercury was thus determined and from a knowledge of the true compressibility of mercury the volume increase of the container with pressure was calculated. The agreement of the volume increase computed and found experimentally is seen (Table I) to be in fair agreement. It was necessary, however, in the course of the measurements to go to termperatures where, owing to the lack of reliable compressibility data for mercury at high temperature, it was impractical to use mercury to determine experimentally the volume increase with pressure. The procedure adopted was therefore to compute the volume increase by the elasticity theory as described at all temperatures but the difference between the experimentally determined value of the volume increase and that computed at ordinary temperatures was applied throughout the temperature range of experiment. This amounts quite approximately to using the experimental value at ordinary temperatures and computing the increase of the quantity with temperature by elasticity theory using the elastic constants appropriate to the higher temperatures. The error introduced by entirely neglecting the variation of volume increase with pressure for No. 1 Ni container amounted as a matter of fact to 0.1% at the higher pressure range of measurements, 300 atmospheres.

The temperature expansivity of the container is a quantity which should be known with certainty. Reliance for the expansivity of nickel was placed upon the measurements reported in the Bureau of Standards Scientific Paper No. 426. The results were used by Doctor L. B. Smith to compute the constants of the empirical formula $l = l_0 + a_1 t + a_2 t^2 + a_3 t^3$. The mean value of the quantity measured between t_1 and t_2 is given by

$$\frac{1}{t_1 - t_2}\int_{t_1}^{t_2}\left(\frac{\partial l}{\partial t}\right)dt = l = l_0 + \frac{a_1}{2}(t_1 + t_2) + \frac{a_2}{3}\frac{t_1^3 - t_2^3}{t_1 - t_2} + \frac{a_3}{4}\frac{t_1^4 - t_2^4}{t_1 - t_2}$$

It will be perceived by the use of the formula of Table II that the effect of an uncertainty of one percent in the expansion coefficient introduces an error of roughly 0.018 percent or one part in 5500 at 400°, in the determination of the volume of the container contents in passing from 0° to 400° C.

The interior surface of the container to a considerable depth is under high tension at the maximum pressures and since the coefficient of temperature expansion determined at one atmosphere was employed an error is involved in assuming that the latter applies under the pressures of the actual steam measurements. The temperature expansivity of liquid mercury is known[20] to diminish under pressure and undoubtedly the expansivity of nickel is slightly greater under the tensions which existed in our measurements. The effects appeared too complicated and available data too meagre, however, to attempt an evaluation of their magnitude and the one atmosphere expansivity was applied throughout in reducing the measurements.[21]

TABLE I.

CONSTANTS FOR NICKEL CONTAINER No. 1.

	Volume at 0°	219.642 ± 0.012	
	$r_0 = 4.228$ cm.	$r_i = 2.614$ cm.	
	Poisson's ratio	0.33	
$t°$ C.	Young's Modulus kg./cm.$^2 \times 10^{-6}$	Formula 1 ΔV	Stretch cm.^{3} per 100 atm. From Comp. of mercury.
30	2.183	.0526	.0535
100	2.138	.0541	.0559
200	2.082	.0568	.0541
250	1.984	.0585	Above 200°
300	1.884	.0616	nickel amalgamated
350	1.680	.0691	with the mercury.
400	1.600	.0725	
450	1.400	.0829	

The compressibility of mercury used in deducing the "stretch" of the container was:[22]

[20] P. W. Bridgman, Proc. Amer. Acad. Arts and Sci. *47*, 345 (1911).

[21] K. T. Compton and D. B. Webster, Phys. Rev. *15*, 159 (1915), showed that the temperature dilation of piano wire increased 0.54 per cent when the load on a 0.0310 cm. wire was increased from 4.5 kg. to 9.5 kg.

[22] Carnazzi, Cim. (5) *5*, 180 (1903).

$\beta \times 10^6$	22.8°	52.8°	84.8°	110°	150.3°	191.8°
1 − 500 atm.	3.8	3.9	4.0	4.1	4.4	4.6

The measurement of the total volume of the containers used in the steam experimentation was carried out by evacuating the containers and filling with mercury and with water at the temperature of melting ice. The usual and well known precautions in determining volumes by this method were of course adopted. For weighing the containers a large Gurley balance capable of taking a load of 35 kilos (at this load sensitive to 5 milligrams) was employed. In Table II there is tabulated the volumes of the containers used. It is believed that the volumes are reliable to about one in ten thousand relative to the accepted densities of mercury and water. The values of the elastic constants and thermal expansion are also given in the table.

A detail of some importance is worth mentioning in connection with the calibration of the containers using mercury. The normal vapor pressure of mercury at 360° is one atmosphere and evidently no trace of mercury must be allowed to remain in the containers during measurements of steam pressures. On the other hand if the closure, piece *E*, for example, of the nickel container was removed for removing traces of mercury, it would be difficult or impossible to reestablish the closure without disturbing the volume of the container. Of course the determination of volumes could be carried out after having made a series of steam measurements, but in the event of an accident to the container in the course of a "run" it might be found impossible to reduce the measurements taken prior to the accident. As a matter of fact experience showed that the mercury could be run out very completely leaving only a matter of milligrams of mercury behind. The procedure of passing dry nitrogen into the warmed container by means of a fine capillary passed through the closure piece *E* proved to be satisfactory as a means of evaporating the mercury.

The container of nickel, Fig. 1, was replaced early in 1926 by a pair of containers designed especially for volumes of steam greater than correspond to 20 cc. per gram. At about this time the development, production and knowledge of the physical characteristics of certain alloy steels had progressed to a point where tests of the resistance of the alloys to slight chemical action by water warranted investigation. The nickel container had not on first use proven as satisfactory with respect to its resistance to attack as had been hoped, although after an initial oxide skin had formed, the behavior of this container appeared to be satisfactory. It was found, however, in the case of

machinery steel that a slow and very regular apparent loss of water from the container took place and this was definitely traced to the formation of an oxide film which reduced the rate of decomposition of the water to the rate at which the hydrogen was absorbed by the steel. The observed properties of the steam were then quite approximately a regular and calculable function of time and allowance for the water loss was made. Needless to state, however, many hours of time consumed in making measurements were lost because of the reaction of the water with the container.

While the oxide film in the interior of the No. 1 nickel container, was sufficient to retard water decomposition it should be stated that the mechanical properties of pure nickel are far from satisfactory for pressure work. Upon long heating at high temperatures the metal tends to crystallize and it flows or "creeps" excessively under stress. This is not serious as far as the constancy of the working space of the container is concerned at the upper pressures of the steam investigation, but the threads at the closure tend to yield and the locking nut requires taking up frequently.

The choice of the spherical form for the second container was dictated partly by the fact that the dilation by pressure is small and easily computed by the formula:

$$\triangle V = V \frac{3(1 - 2\sigma)}{E} \frac{p_i r_i^3 - p_0 r_0^3}{r_0^3 - r_i^3} \tag{2}$$

The method of construction will be clear from Fig. 3 which shows two hemispheres C and E machined to fit together, D, leaving a V shaped groove to facilitate the welding together of the two portions. The piece at F was cut off subsequently and used to determine the temperature dilation of the alloy. The method of closure is the same in principle as described, A and B Fig. 2, for the case of the nickel container. The possession of duplicate containers made it possible to save much time since one sphere could be prepared and loaded with a water sample while the second was in use for making measurements.

The thoroughly annealed machinery steel used for the second container was not satisfactory from the point of view of resistance to chemical reaction. At higher temperatures (200°) the hydrogen attained a pressure of 0.2 atms. It was found, however, on subsequent examination that in exhausting the No. 2 container at 350° preparatory to loading with water the protective oxide film which had

been purposely formed prior to use as a protective coating had been entirely removed or decomposed during the course of the heating and pumping. This was somewhat astonishing since preliminary calculation had seemed to indicate that the vapor pressure of the oxygen over the oxide was low enough at 360° to insure a sufficiently low rate of oxide decomposition. However the spongy surface of iron resulting from this decomposition proved, as might in fact be anticipated, to be extremely reactive and enough hydrogen was collected to make identification positive. By lowering the temperature at which the exhaustion of the container was carried out it was found possible to preserve the oxide film intact and hydrogen evolution during steam measurements ceased. Contrary to the experience with the nickel container, however, it was found that decomposition of water had not really stopped entirely, but that the hydrogen was absorbed by the steel as rapidly as generated. By keeping careful account of the time, it was nevertheless possible to apply corrections for the regular loss of water due to gradual oxide formation.

By this time (1930) so-called Nirosta steel (18 percent Chromium, 8 percent Nickel) in large homogeneous ingots became available and after some initial difficulties incident to inexperience in machining the alloy, a pair of containers similar in form and content to the No 2 machinery steel containers was completed. The welding of the hemispheres proved impossible using oxygen-acetylene, but thanks to the General Electric Company their atomic-hydrogen welding process proved entirely successful and two very perfect containers became available. The coefficient of expansion with temperature of the alloy as determined on samples cut from the *F* portion (Fig. 3) are given in Table II. With Nirosta steel the range of temperature in the measurements was extended to 460° C.

During the course of the time the Nirosta containers were under construction a chrome-vanadium steel container similar in every way to the nickel container was constructed, Container No. 1A. This was used to make repeat measurements on liquid water compressibilities up to the critical region, 374° C. Finally a third cylindrical type of container of Nirosta steel, No. 1B, was constructed and used for repeat measurements on water at high densities.

By way of résumé, there were three forms of container used in the steam investigation, the cylindrical No. 1 (Fig. 1) of nickel, No. 1A of chrome-vanadium alloy steel (about 216.7 cc. capacity), and No. 1B of Nirosta steel (about 286.2 cc. capacity); No. 2A, spherical type of

Nirosta alloy steel similar to No. 2 machinery steel container. Finally a small Nirosta steel cylinder was used in vapor pressure measurements. The cylindrical form was used for the measurement of volumes not greater than corresponds to a specific volume of 20 cc. per gram. The spherical type, roughly 550 cc. total volume, was used for the range 20 cc. per gram to 150 cc. per gram. The latter is the saturation volume of steam at about 191.9° C, a little higher temperature than the limit of the explored region prior to 1920. The Nirosta or 18 percent chromium—8 percent nickel alloy, in use for many months con-

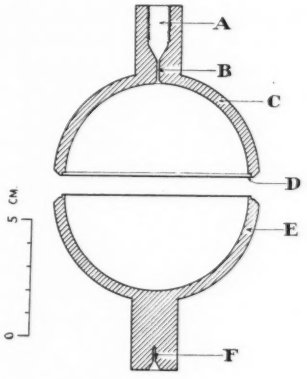

FIG. 3.

tinuously at temperatures as high as 460° C, showed very slight or practically no signs of chemical interaction with water. The coefficient of expansion is considerably greater than either nickel or machinery steel, but on the other hand the expansivity is regular and reproducible. Table II summarizes the data pertaining to the containers.

The heat treatment employed with the chrome-vanadium steel was not extended beyond the point where it could be readily machined. In the case of the Nirosta steel it was heated to about 1200° C and quenched thereby leaving it in a condition for machining without too great difficulty.

The capillary connecting tube between the container and the volume measuring portion of the steam in the earlier series of measurements was of nickel. The nickel capillary proved, however, to be

TABLE II.

DATA PERTAINING TO CONTAINERS USED.

Container	$E \times 10^{-6}$ $\frac{Kg}{cm.^2}$	σ	V_0(Hg)	V_0(H_2O)	At 200° Stretch 100 atm. Eq. 1 or 2
No. 1 Nickel Cyl.	Table 1	0.33	219.642 ± 0.012		.0568
No. 1A Chrome-Vanadium Cyl.	2.17	0.33		216.661 ± 0.005	.0469
No. 1B Nirosta 18/8 Cyl.	2.00	0.28		286.165 ± 0.013	.0649
No. 2 Mach. St. Sphere	2.17	0.30	546.708 ± 0.006		.0966
No. 2′ Mach. St. Sphere	2.17	0.30	550.028 ± 0.008		.0966
No. 2B Nirosta 18/8 Sphere	2.00	0.28	542.881 ± 0.006		.0857
No. 2B′ Nirosta 18/8 Sphere	2.00	0.28	539.023 ± 0.004		.0857
No. 3B Nirosta small Cyl.				7–8 cc.	

V_t (Nickel = V_0 $(1.0000 + 3.95 \times 10^{-5}t + 1.252 \times 10^{-8}t^2)$.[23]

V_t (Mach. steel) = V_0 $(1.0000 + 3.342 \times 10^{-5}t + 3.123 \times 10^{-8}t^2 - 2.109 \times 10^{-11}t^3)$.[24]

V_t (Chrome-vanadium = V_0 $(1.0000 + 3.666 \times 10^{-5}t + 1.338 \times 10^{-8}t^2 - 1.215 \times 10^{-11}t^3)$.[24]

V_t (Nirosta 18/8) = V_0 $(1.0000 + 4.815 \times 10^{-5}t + 1.818 \times 10^{-8}t^2 - 1.335 \times 10^{-11}t^3)$.[24]

[23] Dr. Leighton B. Smith obtained this equation from a formulation of the nickel data contained in Paper No. 426, U. S. Bur. of Standards, 1922.

[24] The expansion coefficients were measured by Doctor Smith using the Pulfrich interferometer apparatus operating on specimens cut from the container and the data formulated by the least square procedure.

Compositions of Steels. The nickel was analyzed by Professor L. F. Hamilton who found as follows: cobalt 0.46, iron 0.31, carbon 0.13, copper 0.12, manganese 0.081, sulfur 0.009, silicon 0.098. The Nirosta steel contained chromium 18.0, nickel 8.00, carbon 0.15. The Chrome-vanadium steel contains carbon 0.34, manganese 0.73, phosphorus and sulphur each 0.019, chromium 0.92, vanadium 0.21.

subject to longitudinal imperfections resulting in such a large number of failures that mild seamless steel was substituted until finally Nirosta capillary tubing was produced by the Summerill Tube Company of Bridgeport, Pa. The steel capillary proved to be troublesome for the bore 0.6 mm. was so small that in time it became stopped due to gradual oxidation of the inner walls at the portion submerged in the high temperature bath. The Nirosta capillary on the other hand was highly satisfactory in every way.

(5) The Thermometers.

The scale of temperature on which it would be desirable to report the steam data is of course the absolute, or thermodynamic scale (Kelvin Scale). Unfortunately the relation of the latter scale to the indications of the several practical or secondary temperature measuring devices is not yet known to the degree of exactness that is commensurate with the reproducibility and sensitiveness of the platinum resistance thermometer, 0.001° C. It is, in fact, not difficult now for investigators working in different laboratories to construct platinum resistance thermometers which will indicate, for example, the normal boiling temperature of the same sample of benzophenone (employing of course perfected designs of boiling point apparatus) in agreement within at least 0.01° or 0.02° C.

The perfection in the construction and use of platinum resistance thermometers sensitive to 0.001° C has proceeded parallel with the improvements in the construction and mode of operation of the apparatus used for the fixed points until it is relatively easy to maintain and reproduce the temperature of boiling water and sulfur to about ± 0.001° C and ± 0.013 respectively. On the other hand the reproducibility of the normal sulfur boiling temperature on the hydrogen or nitrogen gas scale as determined by various independent investigators shows a lack of accord which amounts in some instances to tenths of a degree.

At present the standard practice is to determine the electrical resistance of the platinum-resistance thermometer at three temperatures, namely: the equilibrium temperature of water, saturated with air, and ice at one atmosphere; the international-atmosphere boiling point of water; and the normal boiling point of sulfur. These three temperatures are by international convention and agreement of 1927[25]

[25] Burgess, U. S. Bur. of Stand. Jour. of Research, Re. Paper No. 22, p. 635, Oct. 1928.

assigned the values 0° C, 100° C, and 444.6° C and employed to compute the value of δ in the Callendar interpolation formula:

$$t - (pt) = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \tag{3}$$

where t is the absolute or thermodynamic temperature on the centigrade scale and (pt) the "temperature" defined in terms of the resistance of the platinum thermometer by the formula:

$$(pt) = \frac{100(R - R_0)}{R_{100} - R_0}$$

R, R_0 and R_{100} representing the resistance at temperature t, the ice freezing point and normal boiling point of water. The Callendar formula is equivalent to the assumption that the relation between thermodynamic temperature and the electrical resistance of pure platinum is given by the quadratic expression:

$$R = R_0(1 + At + Bt^2)$$

It is to be emphasized however, that no sufficient knowledge is yet available for establishing the validity of the quadratic relationship since in practice t is not known on the thermodynamic scale.

Clearly, two major difficulties arise when the relation between this particular scale of the platinum resistance thermometer and the true thermodynamic scale is sought. The first difficulty is the defect in precision with which the normal sulfur boiling temperature is known, admittedly uncertain by perhaps as much as 0.1° C. The second has to do with the sufficiency of the empirical formula (3) as an interpolation formula. Little can be stated to inspire complete confidence[26] in the use of formula (3) for it is well known that it fails below 0° C where gas thermometry has reached a degree of refinement surpassing that attained above zero.

The scale of temperature uniformly adopted for the steam investigations is that of the platinum-resistance thermometer constructed of pure platinum having a mean temperature coefficient between 0° and 100° greater than 0.00391. The Callendar formula (3) is used for interpolation and the value of δ determined in accordance with the afore-mentioned 1927 International scale specifications.

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[26] Burgess, Le Chatlier, "Measurement of High Termperature" John Wiley and Sons, 1912, p. 199.

Because of the unsatisfactory state of knowledge with respect to the relation between the highly perfected platinum-resistance thermometer and the thermodynamic scale of temperature an extensively planned investigation of the subject was undertaken in 1920 in this laboratory. The investigations initiated under the program are beginning to provide very consistant data encouraging the belief that a body of information will become available pertaining to important details bearing on the behavior of the platinum-resistance thermometer and its relation to the several gas scales of temperature. The data required to reduce the gas scale readings to the thermodynamic scale of temperature are also being obtained by three independent methods.

It is hoped that similar gas thermometric investigations may soon be undertaken in other laboratories in order that the present lack of positive knowledge regarding the relation of the platinum resistance scale to the absolute temperature scale may be reduced. This is greatly to be desired for a final statement regarding the consistency of the great body of steam measurements which is nearing completion cannot be written until the present clouds over the temperature scale situation are cleared.

An example of the nature of the difficulty of comparing data from different experimental sources by means of the two empirical principles of thermodynamics may suffice to illustrate the importance of the temperature scale problem. N. S. Osborne, H. F. Stimson and E. F. Fioch[27] have completed extremely precise measurements of the latent heat of evaporation of liquid water from 50° to 270° C. The measurements at the Massachusetts Institute of Technology on the other hand have provided values for the relation between saturation pressure, temperature and specific volumes which may be used to compute latent heats by means of the thermodynamic formula of Clapeyron $L_e = T\frac{dp}{dT}(v_1 - v_2)$ where T is the thermodynamic temperature and p, v_1 and v_2 the pressure and volumes of unit mass of the vapor and liquid determined at T on the thermodynamic scale of temperature. Now to obtain $\frac{dp}{dT}$ the operation of differentiation, or its equivalent, must be carried out on the expression relating the saturation pressure to the thermodynamic temperature. If, however, in

[27] Trans. of Am. Soc. Mech. Eng. *52*, 191 (1930).

place of the true thermodynamic temperature T an approximation to the thermodynamic scale of temperature, say Θ scale is used to relate pressure to "temperature" the quantity $\frac{dp}{dT}$ cannot be evaluated without exact knowledge of the relation between T and Θ. The values of v_1 and v_2 will also correspond to the Θ temperature scale. The Clapeyron equation "latent heat" computed is therefore not a true thermodynamic quantity. Clearly then, lack of certainty of the relation of the temperature scale of the thermometers used in the steam investigation to the thermodynamic scale of termperature leads to serious difficulties in comparing directly measured and thermodynamically derived quantities. The nature of the existing temperature scale situation is of a kind that can only be dealt with by the most refined and painstaking investigations conducted preferably by several groups independently.

One other example of the fundamental importance of an improved knowledge of the relation of the accepted scale of temperature to the thermodynamic scale is of immediate interest. The heat capacity of steam in the vapor or gaseous phase has been determined experimentally by Knoblauch and Koch.[28] The pressure-volume-temperature properties of the same phase have also been measured in the course of the M. I. T. investigation. From the latter data the values of $\left(\frac{\partial^2 v}{\partial T^2}\right)_p$ can be evaluated and if the temperature scale used to relate v to temperature at constant pressure is on the thermodynamic scale of temperature then a comparison of the experimentally determined heat capacity data may be made with similar values computed from the expression $c_p = c_{p_0} - T\int\left(\frac{\partial^2 v}{\partial T^2}\right)_p dp$. In the latter expression c_{p_0} represents the heat capacity for the gas at very low (zero) pressure, a pure temperature function. A cursory survey of the Koch c_p values shows that for important regions of the c_p, T plane the value of the second term of the right hand member of the above equation is several times as large as c_{p_0}. It is therefore clear that an important test of the consistency of the Koch c_p values and the present pressure-volume-temperature data becomes possible only when v can be related to the thermodynamic temperature because the evaluation of a second derivative may be brought into grave error by what may appear to be a slight trend in the relation of volume to temperature in the primary data. In other words the formula

[28] Knoblauch and Koch, Zeit. d. Ver. Deutch Ing. *72*, 1733 (1928).

$$c_p = c_{p_0} - T \int \left(\frac{\partial^2 v}{\partial T^2} \right)_p dp$$

has precise meaning only when T is true thermodynamic or Kelvin scale temperature.

There were five platinum resistance thermometers used in the M. I. T. steam investigation since experimental work started early in 1922. Owing to the world wide disturbance of industry by the war satisfactory pure platinum wire for the thermometers was practically impossible to obtain for some years subsequent to 1919. Samples obtained from 1919 to 1922 from England, Germany and the United States proved of very mediocre quality but the best of that obtainable had to be employed. Thermometer No. 1 was of the flat calorimetric four-lead type with copper leads. The steel thermometer case was filled with dry hydrogen and sealed. The method of aging or conditioning thermometers employed at this laboratory at the time was to heat them to about 500° C and to cool in liquid air repeatedly until the ice point remained unchanged. The calibration points employed (1922) were ice, boiling water, naphthalene and benzophenone, the values for the two latter fixed points being taken from determinations made by the U. S. Bureau of Standards. These fixed points were not normal boiling temperatures given by gas thermometer measurement. No. 1 thermometer was used in all measurements made prior to June 15th, 1925. On the latter date a leak in the iron case was discovered which had evidently occurred at a time sufficiently in advance of June 15th to admit air and oxidize one of the copper leads. By this time, however, the deficiency in quality of platinum had become increasingly exasperating not alone in the steam investigation, but in several other investigations in progress in the laboratory. The Bureau of Standards had earlier undertaken the problem of platinum purification and a supply sufficient for a number of thermometers was finally secured. The quality of this platinum has proved to be everything that could be desired. Over forty thermometers of different types have been constructed for the various investigations of the laboratory and subjected to careful test and control. The experience gained induces the belief that no better quality of platinum has ever been employed in constructing platinum resistance thermometers.

Thermometer No. 2 B. S. was of the flat type made of the Bureau of Standards platinum and having pure gold leads. Aging and calibration was carried out as in the case of No. 1 thermometer except that the sulfur boiling point (444.6° N. P.) was used in determining

the δ of the formula (3). In order to interpret the temperature readings of the No. 1 thermometer in terms of the No. 2 B. S. instrument constructed of the superior Bureau of Standards platinum wire, comparison was made with a duplicate of the No. 1 thermometer constructed and used by Mr. Charles K. Lawrence in his measurement of some properties of amonia.

About January 1926, a leak developed in the case of thermometer No. 2 B. S. admitting water. No. 3 B. S. thermometer was of the strain free type inclosed in a steel sheath. During the aging and calibration process the indications of the thermometer became somewhat erratic and it was discarded.

Two new strain-free thermometers were next constructed, No. 4 B. S and No. 5 B. S., both of the strain-free type with pure gold leads and encased in pyrex glass. Both thermometers were aged and calibrated using sulfur N. B. P. 444.6° [29] as the high temperature fixed point substance. The thermometers were calibrated and used in close-fitting thin-walled nickel protecting sheaths. Each was compared directly and at numerous points with the Lawrence duplicate of thermometer No. 1. The No. 5 thermometer has been held as a reserve and No. 4 used in the course of observations of steam properties. The constants of the thermometers are given in Table III.

TABLE III.

PLATINUM RESISTANCE THERMOMETERS.

	R_0	R_{100}	$(R_{100} - R_0)/100R_0 \times 10^3$	δ
No. 1	17.0889	23.7164	3.878	1.504
No. 2 B S	16.8063	23.4030	3.925	1.491
No. 3 B S strain-free	20.1310	27.9968	3.907	1.52*
No. 4 B S " "	18.2320	25.3831	3.92228	1.4965
No. 5 B S " "	17.6679	24.5917	3.91886	1.5002

* Contaminated wire.

The resistance of the thermometers was measured with a Mueller[30] bridge manufactured by the Leeds and Northrup Company in 1920. The bridge was built into the laboratory type of bridge thermostat and during more than ten years the bridge coils have not at any time

[29] The form of sulfur bath in use in this laboratory has not been described. The sulfur is contained in pyrex glass and electrically heated. The thermometers are of course shielded.

[30] Mueller, Bureau of Standards Scientific Paper No. 228.

differed in temperature more than a few degrees from 30° C. The coils were calibrated in terms of the 10 ohm coil in January 1922, January 1926, and September 1931 by means of a Carey Foster bridge modified for convenience to facilitate bridge calibrations. The change in the bridge coils with time between the first and second calibrations was 0.04 percent and between the second and third 0.01 percent.

The temperatures reported in the M. I. T. investigation may be regarded as all on the scale of the No. 4 platinum resistance thermometer using for interpolation the Callendar formula 3 and the fixed points and recommendations of 1927 defining the international scale of temperature. The readings of the thermometer No. 1 were corrected as has been described by 10° comparisons between a duplicate designated the Lawrence thermometer, and the No. 4 and No. 5 thermometers.

(6) The Pressure Gauge.

The most reliable and exact measurements of pressure can be made with the floating piston or "dead-weight" type of gauge devised by Amagat.[31] The type in use in this laboratory[32] has been under development since about 1910. The gauge is represented in Fig. 4, which consists of two parts, one an isometric drawing representing the gauge assembly, the second showing the piston block with the pressure shut-off and method of mounting the piston-cylinder in the block.

The principle upon which the gauge is based is that exemplified in determining the weight, applied on a scale pan suspended from the piston, required to equilibrate the force tending to move the piston out of its cylinder. To annul frictional effects the piston must be floating in oil and the details of the scheme by which true equilibrium is determined between the weights and the pressure exerted by the fluid under measurement, is of vital importance. Evidently the force of gravity at the place where the gauge is used must also be known

[31] Meyer, Bur. of Standards Jour. of Research, *6*, 1061 (1931) has written out a brief but interesting history of this type of pressure gauge. The paper gives in addition much interesting information pertaining to a quite different design of precision pressure gauge.

[32] F. G. Keyes and R. B. Brownlee, Thermodynamic Properties of Ammonia, John Wiley and Sons, 1916, p. 11. F. G. Keyes and Jane Dewey, Jour. Opt. Soc. of Am., *14*, 491 (1927). J. A. Beattie and W. L. Edel, Ann. Physik, *11*, 633 (1931). J. A. Beattie and O. C. Bridgeman, Ann. Physik, *12*, 827 (1932).

if comparisons between pressures measured with a piston gauge by different observers in different localities is of importance. The deformation of the piston-cylinder by pressure, by temperature, and due to aging of the material of construction are likewise of essential importance in measurements of precision.

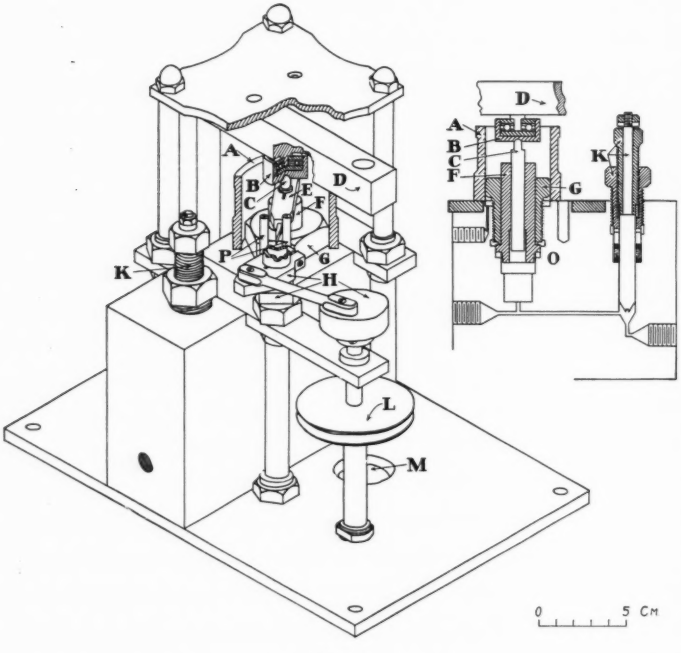

FIG. 4.

The pressure range which the standard four piston R. L. P. C. gauge has been designed to cover is from several to about 1200 atmospheres. If the attempt was made to cover the range with a single piston-cylinder the sensitivity would be less than desirable at low pressures or an inconveniently large amount of weights required at the highest pressures. The design therefore includes four separate piston-cylinder combinations but each cylinder has the same outside

dimensions fitting the gauge block interchangeably. The series of piston-cylinders are designed to have constants of 0.5 mm./g., 1 mm./g., 2 mm./g., and 4 mm./g. The constant is related to the effective piston diameter by the formula:

$$c = \frac{40g}{\pi\rho g_s d_e^2} \quad * \qquad (4)$$

* The value of g at M. I. T. is 980.397.

where g, g_s are the values of the gravitational constant at the place of use, g_s the standard gravitational constant (980.665), ρ the density of mercury in cc./g. at zero degrees, and d_e the effective diameter in cm. The load on the scale pans for the maximum pressure is 250 kilos.

In Fig. 4 the piston of hardened steel is indicated by C, its cylinder by F and the nut locking the cylinder into the block by G. An annealed aluminum gasket is used to seal the cylinder into O its block. The piston supports, through the intermediary of a ball bearing B at its upper end, a cross bar D for the scale pan. The brass collar A is merely an oil catch for the oil accumulating as a consequence of the continuous and necessary leak of oil from the space between the cylinder and its piston. The shut-off K is based on the old standard R. L. P. C. design[33] in use for some twenty years in all pressure work. The design makes it possible for the stem of the valve to move forward and backward through the packing without twist; a point of advantage if the shut-off is to be used frequently at higher pressures. The packing consists of fine woven cotton sheeting material cut on the bias in strips about 2 to 3 cm. in width. It is passed repeatedly through purified ceresin wax held at 110° C until no further air bubbles appear on the material. The strips are then hung to drain and when the wax has solidified the required amount, cut to the desired width (2 to 3 cm.), is wrapped tightly around the piece to be packed. A hard-rubber piece fitting the piston tightly is used at the bottom of the packing gland, the piston with its ceresin packing next and finally a second hard-rubber piece. A steel driving member compresses the packing by means of the nut as depicted. It has always been found that the driving of the packing should proceed by intervals of successive tightenings of the driving nut rather than by attempting to settle the packing into its final state by excessive tightening at once. This is essentially the packing gland scheme that has always

[33] Keyes, Townsend and Young, Jour. Math. and Phys. M. I. T. *1*, 278, fig. 9, (1922).

been used in this laboratory and which has proven serviceable to pressures approaching 2000 atms.

The isometric drawing shows the parts labeled corresponding to the piston-cylinder detail. The letter *E* designates a member clamped to the piston below *B* and serving as a means to oscillate the piston to and fro (30 per minute) by means of the hardened steel rollers *P* actuated by the mechanism *H*, and belt drive to pulley *L*. The holes *M* in the base plate permit the passage of the suspension rods of the scale pan. A hole is provided in the block for a thermometer well and shown in the smaller drawing below the letter *G*.

The first piston-cylinder No. 1 T used in the steam investigation was made by using an automobile motor valve tappet. It was in the form of a cylinder surmounted with a hexagon head having a threaded hole but accurately ground and selected for uniformity of diameter over its entire length. The cylinder was bored and lapped to receive the tappet or piston. The gauge No. 1 T was first calibrated in July 1923 against an open glass mercury manometer 8 meters in length and the constant obtained was 1.01443 mm. per gram at 30° C.

A second calibration in October, 1926, using a jacketed constant temperature column gave a constant 1.015024 mm. per gram at 30° C. Due to grit in the oil the piston of gauge No. 1 was scratched in March 1931. No. 1 T gauge was then replaced by gauge No. 28 constructed in 1923 and having a hardened piston-cylinder made by West and Dodge of Cambridge. Dr. O. C. Bridgeman's calibration of this piston in May, 1927, gave the value 1.99672 mm. per gram at 30° C. By this time, however, data pertaining to a number of gauges had indicated unmistakably that secular changes were taking place in the steel of all the piston-cylinders possessed by the laboratory. Gauge No. 28 on June 16, 1931, was calibrated at the pressure of liquid CO_2[34] at 0° and the constant found to be 1.99770 mm. per gram at 30° C. On June 24, 1931, the constant of gauge No. 1 T was determined at the CO_2 point and the constant found to be 1.015815 mm. at 30° C. The rate of change of the gauges[35] with time is 0.0182 percent per year for No. 1 T in the first period of 3.21 years and 0.0165 percent in the second period of 4.72 years while No. 28 changed on an average by 0.0122 percent from May 1927 to June 1931. Gauge No. 52 having the largest diameter 1.37 cm. has the least yearly change (0.009).

[34] O. C. Bridgeman, J. Am. Chem. Soc. *49*, 1174 (1927).

[35] J. A. Beattie and O. C. Bridgeman, Ann. Physik, *12*, 827 (1932).

The precision of the calibration of the gauges is not inferior to one per twenty thousand and the details of the calibration process are fully described in the references cited in this section.

The device used for detecting the equilibrium is in principle identical with that devised by the writer some twenty years ago.[36] In this scheme the oil of the gauge is separated from the fluid whose pressure is to be measured by a mercury U provided with electrically insulated needles in each arm (J, F Fig. 18). The mercury level in the U is adjusted by means of a small mercury injector piston, H, so that it just makes contact with the needles at zero pressure. Any displacement of the mercury meniscus will evidently cause one or the other of the contacts to break. Thus if a weight is applied to the scale pan in excess of the pressure being measured the gauge oil-mercury meniscus contact will open. If, on the other hand, the weight is too small the other mercury contact will open. The rapidity of operation and sensitivity of the equilibrium detecting device is all that could be desired. The equilibrium obtained therewith is moreover independent of the rate of leak of oil from the crevice between the piston and cylinders. The latest electrical circuit in use for the pressure equilibrium detecting device has been described by Beattie and Edel.[37]

TABLE IV.

Date when Calibrated	Type piston-cylinder	Constant C, mm./gr.	Percent change per year
July 18, 1923	No. 1 T (auto. tappet)	1.014430	
Oct. 4, 1926	No. 1 T (auto. tappet)	1.015024	0.0182
June 24, 1931	No. 1 T (auto. tappet)	1.015815	0.0165
May 1927	No. 28 (made 1923)	1.99672	
June 16, 1931	No. 28 (made 1923)	1.99770	0.0122
May 1927	No. 52	0.499446	
May 1931	No. 52	0.499628	0.009
July 1932	No. 52	0.499681	

Temperature correction of gauge constant $C_t = C_{30}(1 + 2.2 \times 10^{-5}(30 - t))$. Corrections to all pressure observations were applied for the "aging effect" of the piston-cylinders.

[36] See for example Keyes and Brownlee, Thermodynamic Properties of Ammonia, John Wiley and Sons, 1916; also F. G. Keyes, Am. Soc. Refrig. Eng. *1*, 9 (1914).

[37] J. A. Beattie and W. L. Edel, Ann. Physik, *11*, 633 (1932). See Fig. 3, p. 636.

The Table IV summarises the data pertaining to the gauges used in the investigation. All pressures are expressed in international atmospheres or the force per unit area due to a column of mercury at 0° C, 76 cm. in length, the internationally accepted value of the gravitational constant being 980.665 dynes. At this laboratory the gravitational constant is 980.397.

A knowledge of all liquid levels within the apparatus is evidently required before the pressure actually exerted by the fluid of interest under investigation can be stated. The design of the apparatus was executed in such a way that the required liquid levels could be easily and exactly determined.

The oil injector which makes it possible to compensate for the oil escaping from the crevice between the piston and its cylinder has a capacity of about 100 cc. It is represented at *B* in Fig. 5 and the most important detail is the oil tight sliding piston represented in Fig. 5*A*. The screw (18 threads per inch) which advances the oil-pump piston is depicted at *A*; the oil cylinder at *B*, a swivel type joint is provided at *C* and the piece *D* of mild steel should be a fair sliding fit in the uniform lapped hole of the cylinder (clearance about one or two thousandths inch). The end of *D* opposite the joint, *C*, is turned down to 0.65 cm. diameter, leaving it one inch in length. The end is threaded to receive a nut *G* and carefully turned washer *F*. Discs of machinery belt leather 0.3 cm. thick are cut 0.1 cm. larger in diameter than the base of the cylinder and placed on the stem of *D*, represented at *E*, and compressed by means of the nut *G* and washer *F*. The piston *D* is now placed in a lathe and ground true with a tool post grinder until, well oiled, it can be drawn into the cylinder *B* by means of the screw. The torque at the end of the 30 cm. spokes required to draw *D* into the cylinder need not exceed twenty to thirty pounds.

The assembly drawing of the steam apparatus, Fig. 9, illustrates the application of the equilibrium detecting device as it was actually applied in part of the steam investigation. The water sample was here confined by liquid water or by mercury as circumstances required and the two risers were connected to a manifold into which the volumnometer *I* connected. The mercury in riser *H* made connection with the oil line of the gauge, *W*, and was held at the needle point, represented within *H*, by means of an oil injector pump not shown in this drawing (see *B*, Fig. 5).

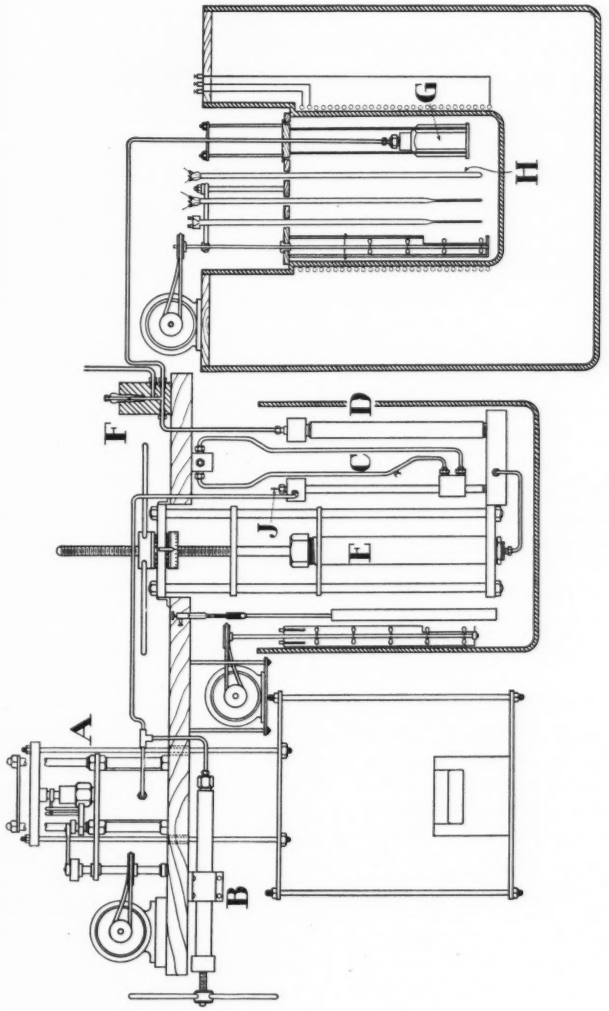

FIG. 5.

(7) Measurement of Volume Changes.

The details of the volumnometer are represented in Figures 5, 6, and 7. Figure 5 represents the apparatus assembly used where mercury and liquid water confine the water sample and *E* shows the volumnometer assembled. It consists of a cylinder of steel which receives a uniformly cylindrical piston of selected drill rod. The packing of the piston to enable it to be displaced without leak or wear is similar in principle to that already described for the stems of pressure valves. Figure 6 shows the detail of the packing gland for the piston of the volumnometer, *F* representing the cylinder. The ceresin packing is represented at *E*, the hard rubber rings at *D*, the driving ring at *C* and the threaded nut used to compress the packing

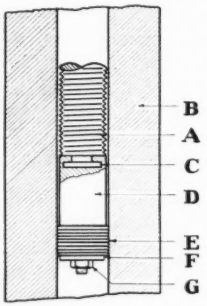

Fig. 5*A*.

by *B*. The piston is designed to allow a clearance of about 0.05 mm. to 0.1 mm. in the cylinder and the hole in the packing nut *B* may be as much as 1.0 mm. larger in diameter than the piston in order to avoid scoring of the piston as it moves to and fro through the nut. In fact it will be evident that the piston should not come in contact with steel except in the case of the driving ring. The latter may have an internal diameter 0.05 to 0.1 mm. greater than the piston diameter and should be made from annealed steel.

In the case of a small volumnometer such as is used in the steam measurements, total displacement 50 cc., a length of drill rod may be selected for the piston, care being exercised to choose a length uniform in external diameter and having a smooth surface. The thread is cut directly at one end of the piston. The type of thread used is of

the so-called trapizoid type represented at G in Fig. 7, which causes the thrust to be taken by thread surfaces perpendicular to the axis of the volumnometer piston. A V thread tends to wedge and brings about increased friction at the higher pressures. Thus at pressures of 350 atm. for which the steam volumnometer was designed the total thrust on the piston is 710 kilos (1570 lbs.) and the trapizoid thread insures that the wear on the piston threads and driving nut F is a minimum. The thread is lubricated with Dixon's graphite grease.

Larger volumnometers (250 cc.) for higher pressures (1500 atm.) have been constructed and used, while one volumnometer of 1000 cc. displacement has been used to 100 atm. It is best with larger diameter

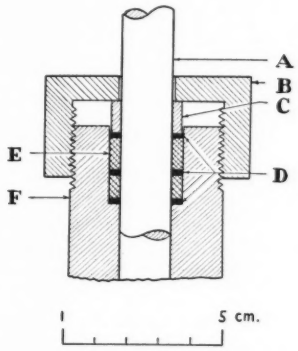

FIG. 6.

pistons to use a large diameter driving thread. The standard practice is to cut the thread on a 5.08 cm. (2 inch) piece of selected drill rod and in the case of a 250 cc. volumnometer to use a 2.22 cm. (7/8″) or 2.54 cm. (1″) piston. One very good method of joining the piston and threaded member is to turn a one degree taper for about 5 cm. on one end of the piston and to bore accurately the end of the threaded portion to correspond, but somewhat deeper than 5 cm. The taper end of the piston is then cooled in liquid air and dropped into the tapered hole. It is well to provide an excised cavity at the bottom of the tapered hole to make certain that the taper end of the piston "clears" and does not come in contact with the bottom of the tapered hole. The contraction of the piston taper in cooling from liquid air

temperatures is of the order of 0.05 mm. If the tapers are accurately prepared and smooth a joint will result which has all the properties that would result were the whole assembly machined from a single

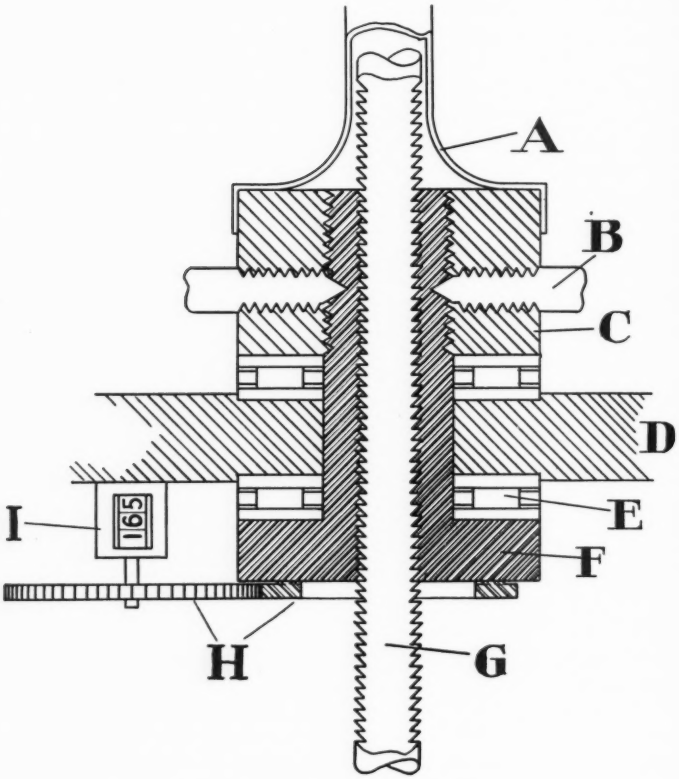

FIG. 7.

piece of stock. It is not practical to turn a volumnometer piston and its thread out of a single bar in the case of the larger pistons because a lathe would be required having an exceptionally long bed. Even if the lathe were available the precautions and time involved to avoid

distortion and deflection of the five foot length of steel during the machining operations become quite formidable. Other methods of joining the two pieces of drill rod stock will occur to the reader, such as threading and pinning; but the method suggested has been used, is satisfactory, and not difficult to execute.

The material of the nut *F* to receive the thread is a matter of considerable importance. Tobin bronze has been found, after some experience, to be the best material. The nut is machined from a solid piece of rolled stock and the operation of thread cutting proceeds quite easily because of the favorable cutting properties of Tobin bronze. Sometimes to insure as perfect a fit as possible I have left the nut thread just short of a final fit and milled the end of the piston screw to form a tap. The finishing cut may then be made by carefully working or tapping with the piston screw through the nut and the result is as perfect a fit as could be desired. A skilled mechanician will, however, have no difficulty in machining the nut with a threading tool to a satisfactory fit. The length of the nut is 5 to 6 times the thread diameter in the case of screws to 2.22 cm. diameter and a somewhat smaller ratio for larger diameter screws.

The bearings for the nut are likewise of great importance and it has been found that the roller thrust bearings manufactured by the Gwilliam Company of Brooklyn, New York, are entirely satisfactory. They consist of two hardened and ground flat steel rings with a bronze cage between, containing hardened steel rollers. The bearings are represented at *E* and one set is used above and one below the frame cross-support member *D*. It will be noted that the hardened rings are set into a recess turned into the member *D* and of course the rings also make a good fit with the barrel of the Tobin bronze nut. The surface of the bronze nut external to the bearing and parallel to the axis is divided into 100 parts and numbered at each 10 marks for use in estimating fractions of a turn. Whole turns are counted by means of a bicycle "cyclometer," *I*, actuated by means of gears, *H*, one of which is secured by screws to the face of *F* perpendicular to the nut axis. A gear having the same number of teeth is of course fitted to the cyclometer shaft.

The locking member *C* is made of steel. After having been adjusted to give the proper bearing adjustment it is bored and threaded on the lateral face to receive the four spokes *B* used both to lock and to operate the nut. In recently executed designs a bevel gear has been fitted to *C* and a motor used to operate the nut.

(8) Calibration of the Volumnometer.

It will be quite obvious that in spite of all care in the choice of a uniform piston the irregularities of the volumnometer piston diameter joined with the inevitable errors of the actuating screw will cause non-uniformity in the volume displacement of the piston. The delivery or volume displacement per turn of the screw will therefore vary as the screw of the volumnometer is moved over its range. The diameter of the piston for the steam work was 1.587 cm. ($\frac{5}{8}$ inch) and possessed 27 cm. of travel. The number of turns per cm. was 7.0866 (18 per inch) and the displacement per turn about 0.28 cm.^{3} The nut periphery divided into 100 parts permitted estimations of 0.001 turn or 0.00028 cm.,^{3} the nominal volume-sensitivity of the volumnometer.

The calibration is carried out with the volumnometer mounted in its position for actual use, exhausted and filled completely with mercury through a 0.06 cm. capillary. A very fine glass capillary is prepared and joined to the end of the steel capillary projecting from the constant temperature bath surrounding the volumnometer. The mercury within the latter is now expelled in five turn portions and weighed. Each portion weighs approximately 19 g. but since the nominal error corresponding to five turns is not inferior to one in five thousand the weight on repeated five turn expulsions of mercury may not be expected to be consistent to better than about four milligrams.

A convenient way of using the data is to divide the total volume by the total number of turns and construct a graph consisting of the differences of the mean volume from the actual volumes as ordinates and turn numbers as absissae. From such a graph the volume displacement from zero to the nth turn may be rapidly computed or the difference in volume between the nth and the $(n + j)$th turn. A convenient way to verify the calibration is to weigh the successive ejections for each ten turns. Fig. 8 is the graph of the calibration for the steam volumnometer. During the calibration it is important that the kerosene bath surrounding the volumnometer should be maintained at constant temperature (30° C is convenient). The degree of regulation required is easily computed for when the volumnometer contains 50 cc. of mercury, 1° C change in temperature will cause the mercury to change volume by 9×10^{-3} cc. The volume displacement for 1/1000th turn is however 0.0003 and accordingly the temperature of the bath must not change by more than 1/30th degree. It is of course quite easy, using steel inclosed mercury regulators, to hold the temperature constant to within $\pm$ 0.005 at 30° C.

A glass tip at the end of the steel capillary leading from the volumnometer must be of fine bore, 0.01 to 0.02 cm., and cut off squarely at the exit. It is well also to arrange for a minimum of exposed or unthermostated capillary, otherwise variations in room temperature will mar the consistency of the weighings. Thus a change of temperature of one degree with one cubic centimeter of unthermostated mercury would cause a volume displacement approaching 1/1000th turn of a $\frac{5}{8}$ inch piston such as used in the steam work.

The mercury must also be ejected very slowly during the calibration, otherwise a rise in pressure will take place within the volumnometer. The isothermal compressibility of mercury is about 3.9×10^{-6} per cm.^{3} or for 50 cc. roughly 2×10^{-4}, about the order of

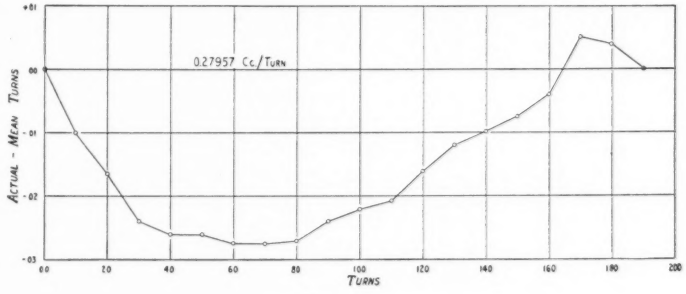

FIG. 8.

sensitivity of the volumnometer. Moreover the conductivity for heat of the body of the latter is finite and on rapid pressure rise there will be an imperfectly adiabatic increase in temperature if the mercury is quickly ejected and then weighed. This effect may, in fact, be important since at 300 K. the temperature rise on adiabatic compression is 0.0032° C per atmosphere. When due care is exercised with respect to the indicated technique of ejecting the mercury and the usual procedures followed in accurate weighing practice, consistent calibrations of ten turn portions to within one in five thousand are easily attained.

In the case of the steam investigation the container volumes are believed to be known to the order of one part in possibly twenty thousand; certainly to one in ten thousand. The total volume of the container, No. 1, Fig. 2 for example, was 219.642 cc. at 0° so that

if this is assumed known to ± 0.01 cc. and the error in the volumnometer for the worst case (50 cc.) contributed an uncertainty of ± 0.01 cc. it would be expected that the error in the total volume measured (220 + 50 cc.) should not exceed ± 0.02 cc. The objective was to measure volumes with a precision of one in ten thousand and this degree of precision appears to have been attained if the con-

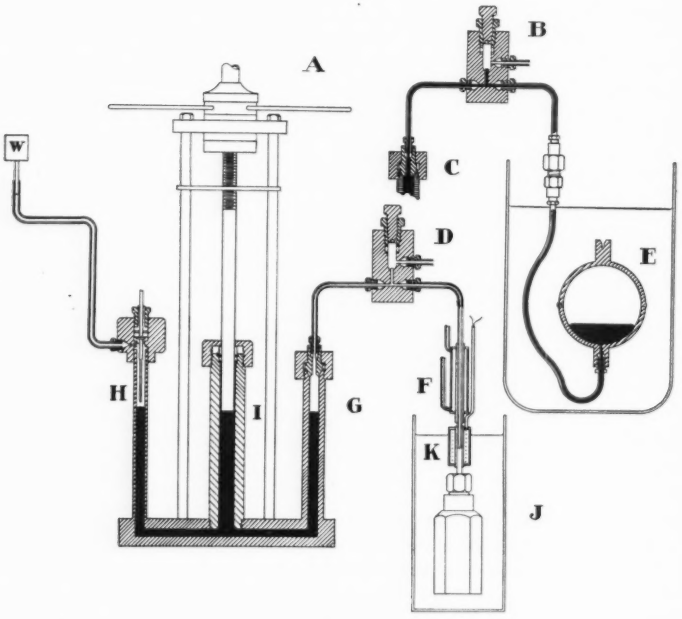

FIG. 9.

sistency of the duplicate measurements for liquid water under pressure are used as a basis for judgment. Of course mere consistency using the same apparatus may be very misleading, but in the case of the volumes of liquid water, duplicate series of measurements using containers of two different metals and different gauges provided data which showed about the agreement anticipated.

Some of the measurements of the volume of the vapor phase of

water were made in the 550 cc. spherical containers using mercury, Fig. 9, *E*, to confine the vapor. *B* is the loading block, *C* the upper part of *G*, while *I*, *H*, and *A* correspond as in Fig. 5. In this case special conditions enter which diminish the precision with which vapor volumes may be determined. In the first place the total mass of water in the container may, at larger specific volumes, exist in relatively appreciable amount on the container walls in the adsorbed state. The amount of water in the latter state will depend of course on the temperature and the pressure, increasing markedly as the temperature is lowered and augmenting with pressure. Because of the adsorptive property of water, volumes corresponding to specific volumes greater than 150 cc. per gram (saturation temperature 191.93° C) were not measured. Nothing, in fact, short of a new method which by its nature is capable of furnishing data independent of the adsorption phenomenon will suffice to give precise values of the volumes of steam at low pressures and temperatures.[38]

A further obstacle to securing exact volume measurements on water vapor at low pressures where mercury confines the fluid resides in the difficulty of correcting the observed volumes or if it is preferred, the observed pressures for the effect of mercury vapor. The effect of the presence of mercury vapor may not be considered allowed for by subtracting from the total pressure the normal equilibrium pressure of mercury vapor at the temperature of experiment. Gibbs[39]

[38] F. G. Keyes and S. C. Collins, Proc. Nat. Acad. Sci. *18*, 328 (1932).

The method described in this paper has since been greatly improved and tested further using gaseous ammonia and carbon dioxide. The indications are that $\left(\frac{\partial H}{\partial p}\right)_T$, $(H = U + pV)$ can be very exactly determined at low temperatures and pressures. The coefficient is equivalent thermodynamically to $\left(\frac{\partial v\tau}{\partial \tau}\right)_p$ where v is volume and τ reciprocal Kelvin temperature. From the empirical but accurate representation of the latter coefficient as a function of temperature and pressure complete information regarding pressure-volume-temperature properties can be obtained. The results obtained by the use of the method are entirely unaffected by adsorption effects. Moreover, while the method is particularly valuable for low pressures, it is not necessarily restricted to this region. However, the low pressure and low temperature range is particularly interesting in the case of steam and measurements are now being made.

[39] J. W. Gibbs, Scientific Papers, Longmans Green and Co., 1906, p. 154, Eq. 272.

proved, and Poynting[40] independently pointed out that the normal equilibrium pressure, vapor pressure, of a subtance was altered when pressure was applied to the condensed phase. Thus if subscripts one and two denote respectively the vapor phase and condensed phase the thermodynamic equation governing the state is:

$$(v_1 dp_1 = v_2 dp_2)_T \tag{5}$$

Using the idealized expression $pv = RT$ for the gas phase and assuming the condensed phase to vary linearly with pressure the following expression for the equilibrium pressure is obtained:

$$p_1 = p_{\text{sat}} \exp\left[\frac{V_0}{RT}(p - p_{\text{sat}}) - \frac{\alpha}{2RT}(p_2 - p_{2_{\text{sat}}})\right] \tag{6}$$

where the volume of the condensed phase is assumed given by $V_0 - \alpha p$. It is evident that the equilibrium pressure, p_1, will always increase since V_0 is necessarily positive, and α small.

The kind of correction here referred to is commonly termed the "partial-pressure-of-mercury" correction, but partial pressure loses meaning as consideration turns from the conception of idealized gas mixtures with constituents behaving as though each produced its pressure effect independently. The equation (6) will therefore be expected, as the temperature rises, to become inexact as a means of correcting for the effect of mercury in an apparatus where the vapor of a substance is confined with mercury as in the case under discussion.

A better approximation to allow for the presence of mercury vapor can be secured only when a knowledge of the properties of mixtures of steam and mercury are available. If the pressure-volume-temperature properties of mercury vapor were known it would be possible to compute the required corrections with some confidence by making use of the body of information now available in connection with the equation of state of pure substances and their mixtures.[41]

The data obtained for the volumes of steam where mercury confined the water (150 cc. to 20 cc. per g.) extend to 330° C. Considerations to be discussed in detail in the paper dealing with superheated steam will indicate that the correction for the mercury-vapor-effect given by Equation (6) suffices to possibly 300° but that significant

[40] Poynting, Phil. Mag., *12*, 32 (1881).

[41] F. G. Keyes and H. G. Burks, J. Am. Chem. Soc., *50*, 1100 (1928). L. J. Gillespie, Phys. Rev., *36*, 121 (1930). H. T. Gerry and L. J. Gillespie, Phys. Rev., *40*, 269 (1932).

error results if Dalton's partial pressure rule is used for correcting the measurements taken above this temperature.

The volume measurements made in the vapor phase corresponding to 50 cc. per gram and less were made by what may be referred to as the "constant-volume-variable-mass" method. Here, Fig. 9, the vapor phase in the container, *J*, was confined by liquid water in the capillary above the level of the constant temperature bath in which the container was supported. The amount of water in the latter is of course determined, with a given total sample of water originally introduced into the system, by the setting of the volumnometer piston. In this way measurements over a range of steam densities can be made. A major difficulty with this method lies however in the definiteness with which the water-liquid-vapor phase meniscus can be located. After considerable experience a capillary heater was designed and constructed by my collaborator, Doctor Leighton B. Smith. The heater represented in Fig. 9 at *K* is adjusted in a position which leaves its lower three fourths submerged below the surface of the bath fluid.

The detailed construction of the heater is made evident in Fig. 10 where *F* represents the capillary connecting the container to the loading block *D* of Fig. 9. The cross section representation shows the capillary at *F* over which is drawn a silver tube *E*. A mica frame perforated with holes *C* to receive wire is constructed as indicated at *D*. The leads from the electrical resistance wire are threaded through a mica strip *B* and insulated from the metal of the case by two mica strips shown in the section drawing. The case *G* is of steel and all joints are silver soldered. The device is important, indeed indispensable where, as quite generally is the case, the fluid under investigation must be confined by the same fluid.

By introducing electrical energy the contents of the capillary can be heated a few degrees above the temperature of the main body of vapor in the container. A cooler, *F*, Fig. 9 through which water is circulated is next placed just above the heater. It will be readily perceived that by this means the meniscus or liquid-vapor-junction in the capillary will be sharpened and the limits of its position fixed, particularly when the vapor in the container is near saturation. The 0.06 cm. capillary had a volume of 0.0029 cm.^{3} per cm. length and if the liquid-vapor junction, as appears to be the case, is localized within $\pm$ 0.5 cm., the error in determining the mass of water in the vapor phase can be stated. At specific volume 20 cc. per g. there would be

about 11 gr. of water in the container No. 1. Using the figure 0.003 cm.^{3} for the uncertainty in locating the capillary liquid-vapor junction it turns out that the vapor density of the container content would be uncertain by about one part in thirty-seven hundred. At higher vapor densities the error in computing the mass of vapor would of course be correspondingly less; at smaller densities on the other hand greater.

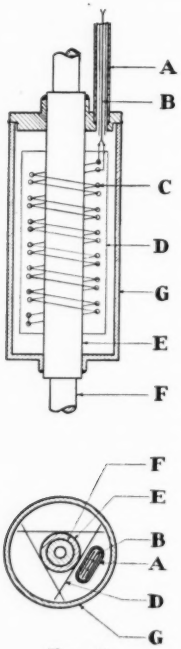

FIG. 10.

The earlier measurements were made without the capillary heater and at temperatures not far from saturation. Long periods were required before equilibrium was attained at the water-vapor junction in the capillary. Even with the exercise of every care it was difficult to be sure that equilibrium existed and it was only after installing the heater that the desired measurements close to saturation could be made.

(9) Dilation of Volumnometer and Other Apparatus Parts Due to Pressure.

The volumnometer and all accessory apparatus parts containing pressure transmitting fluids are kept at constant temperature 30° C during measurements. It is practically impossible to compute the total pressure dilation of the system in the bath but it is quite simple to determine the net pressure-stretch effects experimentally. To do so it is necessary to close off the capillary at the point where the container is attached. The shift in reading of the volumnometer is then determined at various pressures and for pressure increasing and decreasing. The readings should coincide but it is good practice especially after the apparatus has been newly assembled to increase the pressure to a value considerably in excess of the highest pressure to be used subsequently in measurements on the fluid of interest and to maintain the high pressure for a number of hours. This procedure may be described as a "seasoning" operation and it is usually found that on releasing the pressure the packing drive-nut of the volumnometer (*B*), Fig. 6, can be tightened.

After thorough seasoning a series of volumnometer displacements may be taken along the course of rising pressure and followed by similar readings as the pressure is relieved. The two series should be identical to within one or two thousandths of a turn of the volumnometer piston nut. If not, the seasoning should be repeated until accord is obtained but as a rule reproducibility is attained after a thorough seasoning of several hours at twice the upper limit of the pressure it is expected to use in actual measurements on substances.

The simplest manner of using the apparatus dilation measurements is in the form of a graph where the volumnometer readings in turns are recorded as ordinates and the pressures as absissae. Should mercury be added or withdrawn from the system prior to connecting with the container and making measurements on a fluid, a new graph may be constructed, or corrections computed, by making use of the data on the compressibility of mercury by Bridgman[42] $(4.2 \times 10^{-6} - 1.54 \times 10^{-10}p)_{30°}$ (or Carnazzi—Table I) and computing the adjustments required.

The compressibility of the oil (53.1×10^{-6} cc./cc. at 25° C) is not a factor since contact of the mercury is always maintained with the insulated needle used to maintain the location of the mercury-oil

[42] P. W. Bridgman, Int. Crit. Tables, Vol. II; see also Cim. (5) *5*, 180 (1903).

junction at the needle point H, Fig. 9. A slight but usually negligible effect enters in allowing for the oil pressure in computing total pressures since the oil density (0.9083 g/cc. $+ 5.3 \times 10^{-4}t$) increases with pressure.

Another minor factor deserving mention is connected with the finite compressibility of the volumnometer piston.[43] The piston is calibrated at substantially atmospheric pressure but in actual use it is under pressure. The compressibility of steel is however of the order 0.6×10^{-6} and in the case of the steam volumnometer each 100 atmospheres with fifty cubic centimeters of piston exposed to pressure would cause a contraction in piston volume equivalent to about 0.010 turn. In applying this correction it is best to note the piston volume exposed to pressure at the time of the pressure dilation determinations and add the number of turns corresponding to the piston compression for each reading. The equation $(6.0 \times 10^{-7} \cdot \Delta \cdot n \cdot p)$ where Δ is the piston volume per turn in cm.^{3}, n the number of turns reckoned from the zero used in the dilation experiments and p the pressure, can then be used to compute the compression effect for use in reducing actual measurements.

Reference should also be made to the fact that in the measurements using liquid water as the confining fluid for the container contents an exact knowledge is required for the compressibility of water at the temperature 30° C of the volumnometer bath. This is however easily secured by bringing the container completely filled with liquid water to 30° C and measuring the decrease in the number of turns of the volumnometer over the entire range of pressure. After these readings have been corrected for pressure "stretch" of the container, volumnometer and accessory parts, and volumnometer piston compressibility, it is a simple matter to correlate the data and obtain an equation for the volume of water at 30° C as a function of pressure.[44]

During actual measurements the container capillary or rather

[43] The frame rods holding the volumnometer are evidently stretched when the contents are under pressure. It is also evident, however, that this effect is included in the determinations of the "apparatus stretch" due to pressure. Of course a certain displacement of the volumnometer readings under pressure relative to the practically zero-pressure mercury calibration readings enters, but the piston is sufficiently regular to render the volume error of this displacement negligible.

[44] At 30° C between 100 and 200 atm., we obtain a mean diminution of volume for 1 cc. amounting to 43.62×10^{-6} cc. Further data will be given in the paper dealing with the volumes of liquid water.

portions of it will in general be at temperatures up to 10° different from 30°, and accordingly the fluid in the capillary connecting tube will be subject to a temperature gradient. The amount of water in this state is, however, small and it is best to proceed with the reduction of the observations neglecting provisionally the corrections for the compressibility of the connecting tube fluid. The resulting data, while slightly inexact, may than be used to obtain the required true mass of the capillary fluid in each measurement and a final value computed for the amount of substance in the container. As a matter of fact, in the case of water, the compressibility in the range 20° to 50° is almost constant and in the measurements of liquid water volumes under pressure the average value of the compressibility between 20° and 40° suffices for computing the mass of water in the capillary.

(10) Case where Mercury Confines the Water Sample.

The apparatus pressure-stretch data are of course only valid for the quantity of mercury present in the apparatus at the time the data were taken. If mercury is used to confine the water sample *F*, Fig. 9, a part of the mercury will be at the same temperature as the water sample which is of course in the case of water, in general higher than that of the volumnometer bath (30° C). Proper allowance must therefore be made for the temperature dilation of the mercury transferred from the volumnometer to the container and its compressibility. The temperature dilation of mercuty at atmospheric pressure is well known but the compressibility as a function of pressure and temperature is not known over a wide range of temperature. We have used the data given by Carnazzi[45] for the reason that Bridgman's more recent data does not extend to high enough temperatures. There is very great need of a determination of the *p-v-t* properties of liquid mercury over a long temperature and pressure range.

In spite of the fact that the data for liquid mercury are deficient no great error is introduced in measurements where the volume of fluid under measurement is large relative to the volume of mercury in the container. Thus for example, at 150 cc. per gram the 550 cc. container would have about 525 cc. of steam and 25 cc. of mercury contained in it. For a temperature of 300° the difference in compressibility of the mercury from that at the volumnometer temperature would be 1.3×10^{-6} cc. per cc. of mercury. The total volume

[45] Carnazzi, Cim., (5) *5*, 180 (1903).

change of the mercury for a pressure difference of 15 atm. is therefore 5.0×10^{-4} cc. or about 0.0018 piston turns. It is evident from this example that an error of fifty percent in the temperature coefficient of compressibility is not too serious.

The temperature dilation is more important for it is nearly fifty times the compressibility and nothing is known regarding its change with pressure at higher temperatures. The latter is however undoubtedly small. In all work at this laboratory the one atmosphere temperature dilation of mercury has been used.

(11) Preparation of Gas-free Water.

Mere boiling of water in a flask at atmospheric pressure is not sufficient to remove the last traces of dissolved air. Nor will exposing a sample of water to a vacuum at or just above the freezing point (vapor pressure 4.8 mm.) even for considerable time suffice. Prolonged shaking in a discontinuously applied water aspirator pump vacuum will pretty completely remove dissolved air[46] but in the preparation of water for the steam measurements it was more satisfactory to repeatedly distill in vacuum. To follow the reduction in dissolved gas content a gauge of the McLeod type was employed wherein a trapped sample of the gas phase could be compressed to small volume and to pressures when desired several times the vapor pressure of the water. In this way the degree of failure of the vapor sample to collapse completely is a measure of the ratio of gas to water. By the repeated distillation of water in vacuum it was found possible to reduce the volume ratio of permanent gas to water vapor at 20° to much less than 5×10^{-9}. The latter number corresponds to roughly 0.00004 percent of air by weight or roughly one in two and a half million.

The final apparatus used for distilling, testing and loading the larger water samples is represented in Fig. 11. Communication of the entire system with a large capacity oil pump was possible by opening the mercury seal represented at *D*. About one liter of water was contained in the bulbs at *B* where the water could be slowly distilled with intermittent pumping from one bulb to the other as many times as was desired. It will be noted that under certain conditions a value for the gas content determined by the McLeod gauge, *E*, may be a true value for the gauge but not representative of the gas content in the bulbs, *B*. This is particularly likely to be the case during

[46] F. G. Keyes and L. J. Gillespie, Jour. Biol. Chem. *13*, 244 (1912).

active distillation. However, by allowing the system to stand over night the readings at E become independent of time and fairly representative of the essential gas content of the water sample.

(12) METHOD OF LOADING WATER SAMPLES INTO STEEL CONTAINERS.

The loading of the water sample into glass container A Fig. 11 is quite simple. It proceeds by distillation on cooling A with ice water.

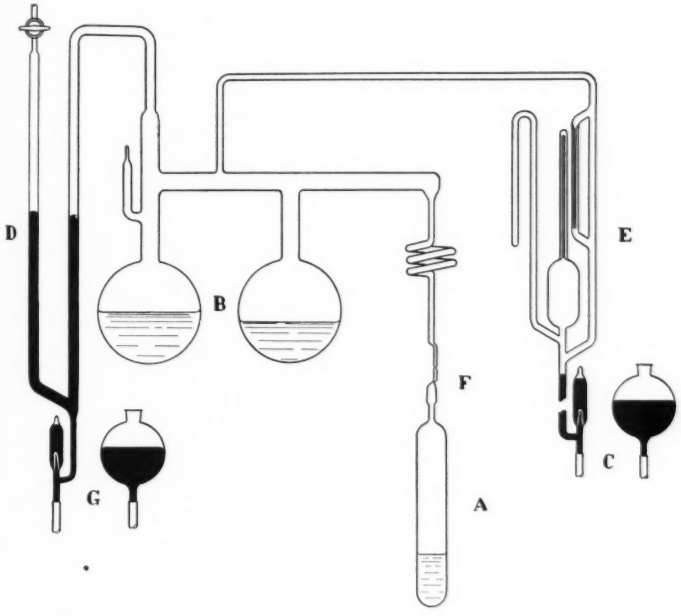

FIG. 11.

Obviously it is necessary to heat A prior to loading in order to free the walls from adsorbed carbon dioxide, air, or other gases. When the desired volume of water (the volume of A as a function of the length being known) is collected, the flask is sealed from the apparatus at F. The weight of water within A can then be exactly determined from the known total weight of the water plus container A after the water has

been transferred. The method of loading the substance sample into the intermediate container has already been described[47] as well as the principle employed to transfer the contents of the latter to the metal container used for the measurements. The method of transfer will be clear from Fig. 12 where *F* the steel capillary leading to the metal container is joined to the glass member of the loading apparatus with de Khotinski cement.[48] Vacuum is applied through cock *E* while *G* is a supplementary tube used in unloading definite amounts of water from the metal container in the course of measurements. After a suitable vacuum has been created in all communicating parts of the loading apparatus the glass container *A* is rotated slightly in the ground joint *B*. By this means the sealed off tip *D* (previously marked with a super-hardened steel edge) is brought into contact with the internal boss *C* and snaps off without fragmentation. The water contents then flow into the metal container and at the proper time the steel shut-off *D* of Fig. 9 on the steel capillary line is closed. The water left clinging to the walls of *A* and in the capillary or other parts of the loading apparatus is removed through cock *E* by means of a pump, the water vapor being held in a weighed trap *H* cooled with liquid air. The method described for transferring substances without contact with air has been used with success in this laboratory for a variety of purposes.[49]

The loading process for smaller quantities of water, 2 grams to 50 grams, and particularly where the material was to be confined with mercury, was carried out with a modification of the apparatus of Fig. 12. The design of the smaller water sample container will be evident from *B*, Fig. 13; a large number of such containers were sealed to a manifold joined to the distillation apparatus, Fig. 11. In this way a series of water samples of proper amount to cover the range of specific volumes from 150 cc. per g. to 20 cc. per g. could be prepared. The glass vessel and its contained water, after weighing, was placed in *A* and the ground glass stopper inserted. The ground joint at *C* is for

[47] F. G. Keyes and W. A. Felsing, J. Am. Chem. Soc., *41*, 599, 604 (1918).

[48] F. G. Keyes, R. S. Taylor and L. B. Smith, Jour. Math. and Phys. M. I. T. *1*, 217 (1922).

A word of caution is worth stating relative to the care in handling water in conatiners where no permanent gas is present. The liquid water behaves in all respects like a piece of steel and will shatter the glass if the position of the container is too quickly reversed.

[49] F. G. Keyes, J. Am. Chem. Soc., *34*, 779 (1912).

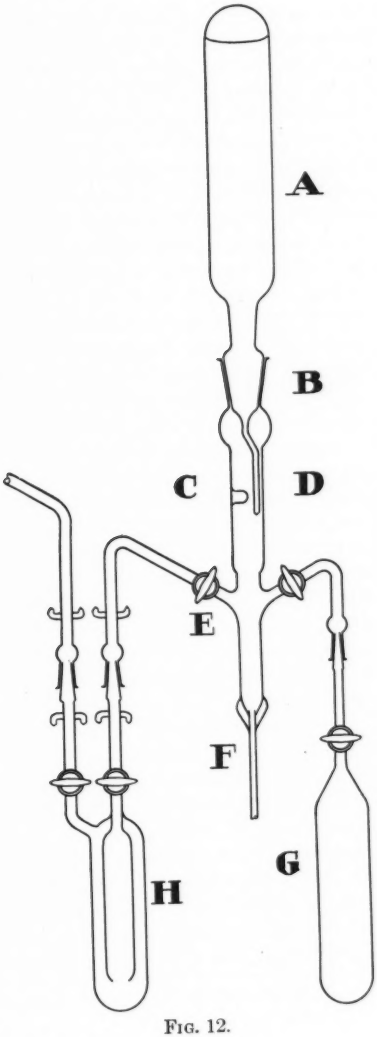

FIG. 12.

rotating the sample holder A, the latter being off-set relative to the ground end. The internal boss D causes the scratched tip of the container B to snap off when A is rotated. The system was pumped out through cock E prior to unloading B.

The Fig. 13 also illustrates the special device used when the water sample subjected to measurement was to be confined with mercury. The disposition and general design of the parts will be evident from the figure.[50] Referring to the figure, G amounts to a screw driver whose shank passes through a packing gland, H. Immediately below the end of the screw driver is a threaded plug bored axially to about 0.15 cm. diameter. The lower end of the hollow plug is prepared for locking against a gold closure disc, K, 0.025 cm. in thickness. When the apparatus is set up for loading J is left screwed off the seat about 0.2 cm. leaving ample opportunity for the water to pass, at the time B is unloaded, along F, past the gold disc and into the container attached to L. The container boss (E, Fig. 9) on the spherical container in the present method of loading is cooled with liquid air, and in this way all the water originally in the container B is transferred to the metal container. The screw driver is finally used to lock the contents of the container by forcing J against the gold closure disc K. The portion of the apparatus carrying the screw driver is now removed and replaced with M; the latter being the connecting means to the volumnometer part of the apparatus.

The volumnometer and connecting tubes when mercury is used to confine the water sample must be filled with a quantity of mercury appropriate to the amount of water in the steel container. After joining the latter to the volumnometer system by means of the cone joint M, the air in the capillary connecting tube is exhausted and the steel cock (B, Fig. 9) connecting therewith closed. Mercury can now be injected into the exhausted capillary by means of the volumnometer and volumnometer readings made at a series of pressures with the mercury in contact with the gold closure disc. These readings are called the "zero-set" readings and by making use of the apparatus pressure-stretch data, the amount of mercury injected by the volumnometer at any pressure and temperature is determined. Communication of the mercury with the interior of the container is readily effected by heating the steel container in its thermostat bath to 200° under a pressure on the mercury side of 50 to 100 atm. In

[50] F. G. Keyes, L. B. Smith and D. B. Joubert, Jour. Math. and Phys. M. I. T., *1*, 191 (1922)—Fig. 3.

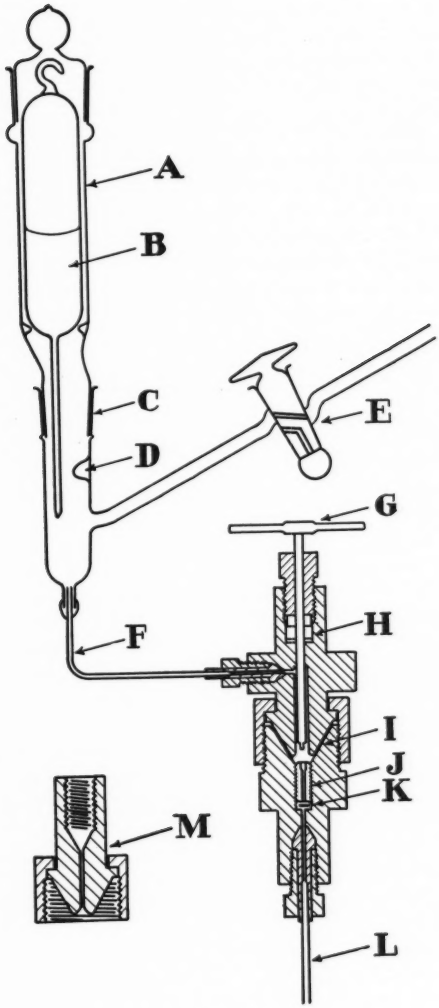

FIG. 13.

this way the gold disc is weakened by amalgamation with mercury and punctured. The disposition of the container in the bath support is shown in Fig. 14, wherein may be seen the stirrer tube and spherical level-indicating steel float for the molten salt bath.

(13) The Constant Temperature Bath.

Constancy of the high temperature bath during measurements is an important matter, and it is not difficult to determine the degree of regulation desirable in measuring, for example, the vapor pressure of water. Thus at 370° C the change of pressure for 1° C is 2.4 atm. and the vapor pressure itself is 207.8 atm. The gauge sensitivity is, say, one in twenty thousand or 0.01 atm. on the vapor pressure. The temperature must therefore not deviate more than 0.004° C or ± 0.002° C.

The construction of automatically regulated baths operating over the range 100° C to 500° C have not so far as known been described until recently although work toward the goal of a bath constant to 0.002° C had been started in 1919. The bath used throughout the steam investigation was built in 1922 and consists of a wrought iron pot wound with swaged iron-clad insulated nichrome wire electrical resistance heaters 15 meters in length. The pot consisted of a 25.4 cm. Shelby seamless tube 45 cm. long with a wrought iron welded bottom. The pot is finally mounted in the center of a large galvanized can leaving about 20 cm. of annular space for asbestos-magnesia heat insulating material. A galvanized iron collar fits the outside top of the pot and makes a driving fit with a wooden annular ring forming the closure for the iron can. The wooden ring at the same time serves as a support for electrical connections, switches, and stirring motor.

Figure 5 shows a cross section of the bath at the right of the figures in which *G* is the nickel No 1 container and *H* the thermostat actuating member. The objects in the bath are all supported from a machined steel cover. The container support is however mounted on a machine disc forming a close fit with the hole bored for its reception in the bath cover. In this way the container may be easily withdrawn without disturbing the heavy bath cover.

The bath fluid consisted of the eutectic mixture of sodium, potassium and lithium nitrates (27.3 percent $LiNO_3$, 18.2 percent $NaNO_3$, and 54.4 percent KNO_3 by weight) fluid at 135° C and entirely serviceable up to 500° C. The material is very clean and highly fluid. When a fresh batch is put into use it is a good plan to place scraps of iron, steel wool or the like in the molten mass. In this way

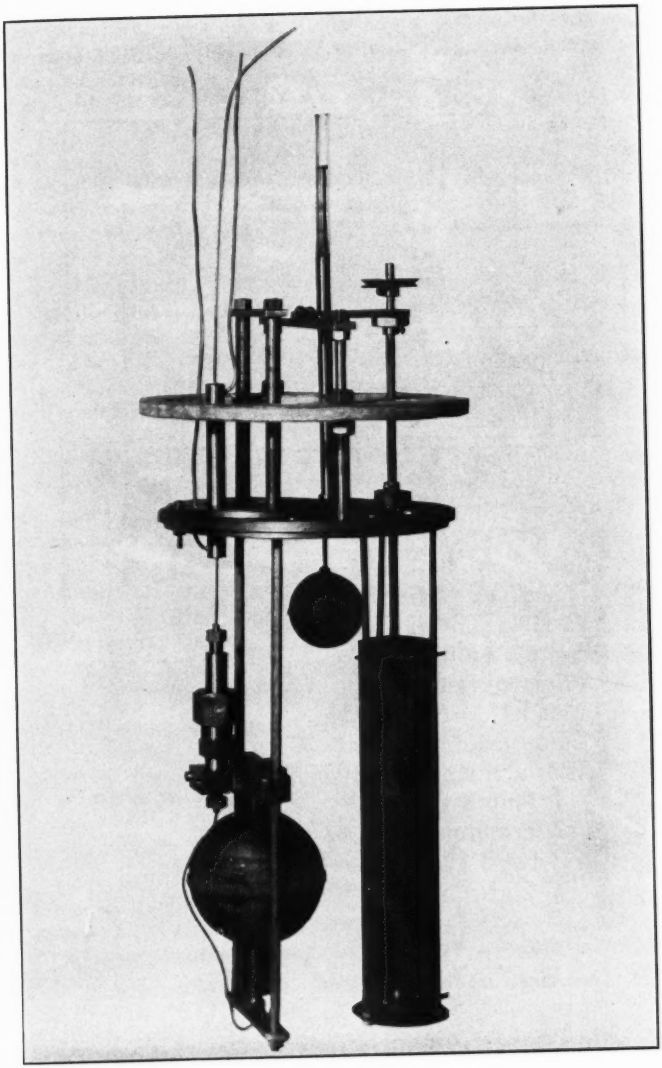

FIG. 14.

it has been found that the mixture loses its power to oxidize steel. The mixture must not be allowed to solidify until all apparatus

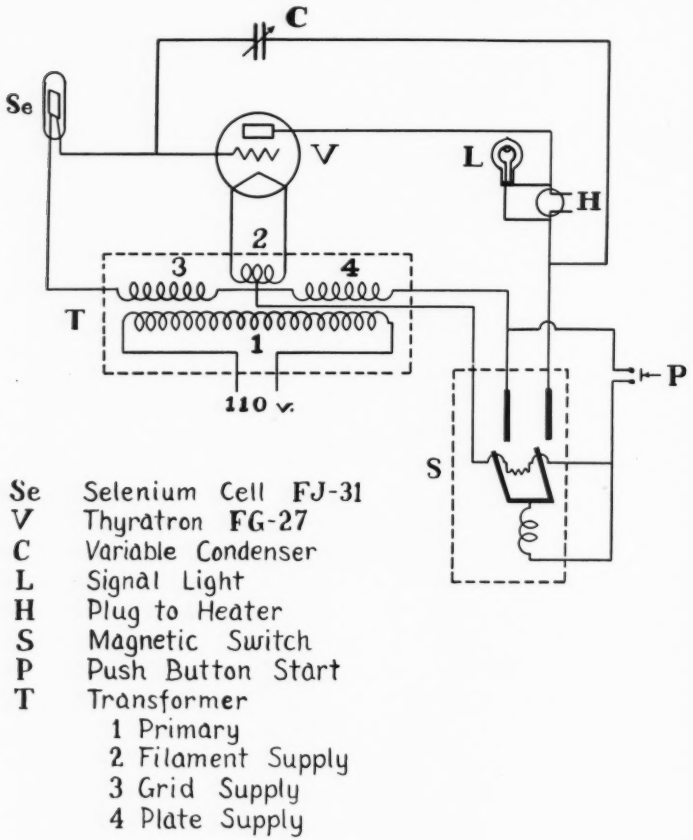

FIG. 15.

objects contained are removed because the mixture contracts to such an extent on cooling that it will, for example, bend or even pull the propellers from the shaft.

The temperature regulation is entirely automatic and the bath element consists essentially of a flat type platinum resistance thermometer of 50 ohms 0° C electrical resistance. The latter or "regulator" is balanced on a Wheatstone bridge and when unbalanced, due to a change in the resistance of the regulator brought about by a change in the bath temperature, a beam of light reflected from the galvanometer mirror falls on a selenium cell. The light falling on the cell causes a relay to act introducing or ceasing to introduce energy into the bath through a small heater placed near the stirrer case. The earlier system has been already described by Doctor L. B. Smith in the annual report printed in Mechanical Engineering, Vol. 48, page 155, with figures 8 and 9. A later and improved design of the bath with full details of the temperature regulation scheme has recently been published by J. A. Beattie.[51] Since the latter publication additional improvements have been made by Doctor Collins and myself enabling automatic regulation to be maintained to ± 0.0005° C. The automatically controlled bath described and used in the steam investigation was continuously improved until toward the beginning of 1926 when bath constancy of ± 0.002° was realized. This degree of constancy is in fact sufficient for the most exacting portions of the steam measurements. The details of the most recent scheme of the automatic regulating circuit will be seen from Fig. 15 and with the notations on the diagram comment is scarcely required.[52]

The thirty degree volumnometer oil bath was automatically controlled by a conventional type of mercury-in-steel regulator. A Beckmann thermometer indicated that extreme fluctuations did not exceed a few thousandths of a degree.

(14) Apparatus Assembly.

The apparatus described in the preceding pages for measuring p-v-T properties is of quite general applicability and is in principle the same as has been used for taking observations extending to about 1500 atm. for some twenty years.[53] There are however various ways

[51] James A. Beattie, Rev. Sci. Instr. *2*, 458 (1931).

[52] In this connection see J. A. Beattie and D. D. Jacobus, J. Phys. Chem., *34*, 1254 (1930).

[53] F. G. Keyes, Am. Soc. Refrig. Eng., *1*, 9 (1914). F. G. Keyes, L. B. Smith and D. B. Joubert, Jour. Math. and Phys. M. I. T., *1*, 191 (1922). F. G. Keyes, R. S. Taylor and L. B. Smith, Jour. Math. and Phys. M. I. T., *1*, 211 (1922). F. G. Keyes and R. B. Brownlee, "Thermodynamic Properties of Ammonia," John Wiley and Sons, 1916.

in which the component parts may be used depending upon the substance and temperature range to be explored. It has already been indicated that to temperatures of 300° mercury may be used to confine the fluid under measurement. At this temperature the vapor pressure of mercury is about 0.324 atm. and because of uncertainty in the corrections to be applied to allow for the "partial-pressure" effect of mercury it is not safe to greatly exceed 300°. For steam at specific volume 150 cc. per gram and 300° the pressure is about 16.61 atm. and accordingly the ratio of the normal equilibrium pressure of mercury to the steam pressure is about one in fifty-one. Of course allowance must be made for the increase in pressure of the mercury due to the pressure of the steam (Poynting effect) but this effect is

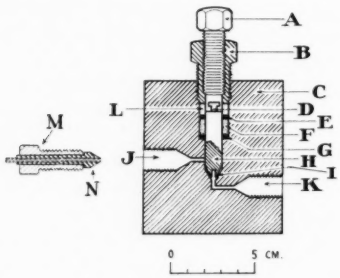

FIG. 16.

only one in four thousand on the total pressure in the preceding example. There must be considered also the failure of Dalton's partial pressure rule already referred to under the section "Calibration of the Volumnometer." The use of Gallium as the confining liquid instead of mercury would be a major improvement for this metal has a negligible vapor pressure at 500°.

At temperatures greater than 300° it is necessary to confine the water with itself. Until the critical temperature is reached however, pressures less than saturation will cause vapor to appear in the container and a two phase junction will make its appearance in the connecting capillary. The exact location of this miniscus junction is a matter of great importance and the heater developed to facilitate its localization has already been described in section eight. The Fig. 5 is a diagram of the assembly as used in the steam investigation but

Fig. 9 indicates the apparatus scheme where mercury confines the water sample.

The shut-off used in the steam investigation* is shown in Fig. 16 where the valve member *H* is made with a cone having a slightly less taper than the seat. A hole is bored in the lower end, *I*, and the edges at the cone are sharp. The design facilitates closure without excessive pressure exerted by means of the member *A*. It is important that the valve part, *H*, should not turn in the packing *E*, *F*, *G*, and to avoid turning a species of universal joint is provided at *D*. The packing is of ceresin impregnated cotton already described. It is compressed by means of the mild steel ring, *L*, driven by the member *B*. The method of making the joints with capillary tubes has already been referred to but at the left of Fig. 16 a detail is given. The cone

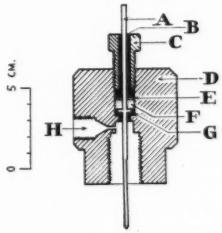

FIG. 17.

ended piece, *N*, is welded over with the acetylene flame and subsequently drilled out to the bore of the capillary. The cone is then dressed to a size slightly sharper than the seat *J*, *K* and driven tight by means of the member *M*. This type of joint is serviceable to pressures of 1000 atm. and has been used with success to about 2000 atm.

The electrical insulating joint is represented in its construction by Fig. 17. For higher pressures, 1000 to 2000 atm., it is best to turn the needle *A* from a single piece of stock. Otherwise the ring on the needle may be silver soldered to the needle. The piece upon which the needle rests, *G*, is of porcelain although hard rubber may be used. *F* is cut from ordinary laboratory rubber stopper. A few discs of mica are provided at *E*. Insulation between the needle stem and the driving screw, *C*, is provided by using hard rubber.

* A later design is shown at K, Fig. 4.

The capillary into which the needle projects is about 0.3 cm. in diameter and *D* may be locked onto the capillary portion by using an annealed aluminum gasket. Capillary tube connections to the gauge or elsewhere are made by the usual cone joint, *M*, *N*, Fig. 16, at *H*. This type of insulating needle is very practical and lasts indefinitely.

(15) Special Apparatus for Most Recent Vapor Pressure Measurements.

Many measurements of the vapor pressure of water were made in the apparatus assembly represented in Figs. 5 and 9. However after continued experience had shown the superiority of Nirosta chrome-nickel steel as a container, a simplified apparatus was assembled during 1932 and used exclusively for vapor pressure measurements. The Fig. 18 indicates the disposition of parts, *E* being the Nirosta cylinder containing the water sample loaded through *C*, and attached to the shut-off block *B*. Varying amounts of water could be introduced at will by operating the volumnometer *I* and forcing water from *G* into the container. In this manner it was possible to wholly collapse the vapor phase in *E* and demonstrate the presence or absence of permanent gas. Moreover when desired water vapor could be removed from *E* by opening the cock at *B* and pumping at *C*.

Liquid water communicated directly with the mercury of the *U* in block *L* and the mercury-water miniscus maintained in position by means of pressure exerted by the oil injector attached to *W*. *F* and *J* are insulating needles and the position of exact contact of the mercury with both needle points could be made before measurements began by means of the mercury injector *H*. The shut-off *K* served to interrupt pressure communication between the water sample and the gauge connected to *W*.

The function of the capillary *U* block *L* is two fold. It serves to separate the oil of the gauge from the water sample and also to indicate when pressure equilibrium has been established in the same way that the mercury-oil miniscus does at *H*, Fig. 9. Thus too great a weight on the gauge scale pan will cause the vapor in *E* to collapse thereby displacing the mercury-oil miniscus in *J*, and making contact at the mercury-water miniscus at *F*. Too little weight on the gauge scale pan on the other hand causes vapor in *E* to be evolved from the liquid phase and the mercury in the *U* block *L* is displaced breaking contact in *F* and making contact in *J*. In this way the *U* acts as a very sensitive detector of pressure equilibrium. It was found in

practice by Doctor Smith that the sharpness of the water-needle contact was affected by the finite electrical conductivity of the water. At a convenient time the water side of the U was disconnected and replaced with oil. The shift of the mercury level in the U with pressure was than determined by means of the mercury injector H.

The sensitivity of the equilibrium detector is readily established as follows. The bore of the capillary containing the insulating needles F, J, Fig. 18, is 0.3 cm. The diameter of the piston of the pressure gauge is 0.682 cm. It has been found by independent trial that $\pm$

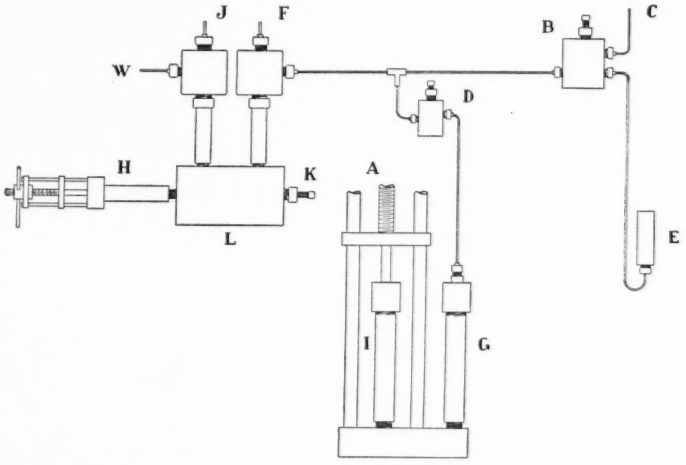

FIG. 18.

0.001 cm. displacement suffices to make or break contact. Therefore a piston movement of $\pm$ 0.0002 cm. will suffice to produce $\pm$ 0.001 cm. motion of the oil-mercury miniscus. With larger diameter pistons the detectable piston movement is less and for piston diameters less than the diameter of the insulated needle capillary the device is less sensitive. It will be observed that the functioning of the detector is independent of oil leak.

The electrical circuit used for the equilibrium detector has been greatly modified during the many years it has been used. The simplest system is the thyratron FG-27 circuit which permits a current

of only 1×10^{-6} amperes to flow from the mercury to the needle. It is essential in any electrical circuit that is used to have a very small current pass the junction for it has been found that too great a current causes the formation of an oil-mercury emulsion at the miniscus which not only diminishes the liquid mercury in the system but causes an uncertain contact.

CAMBRIDGE, MASS.